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THE
SPECTROCHEMICAL ANALYSIS OF METALS AND ALLOYS.

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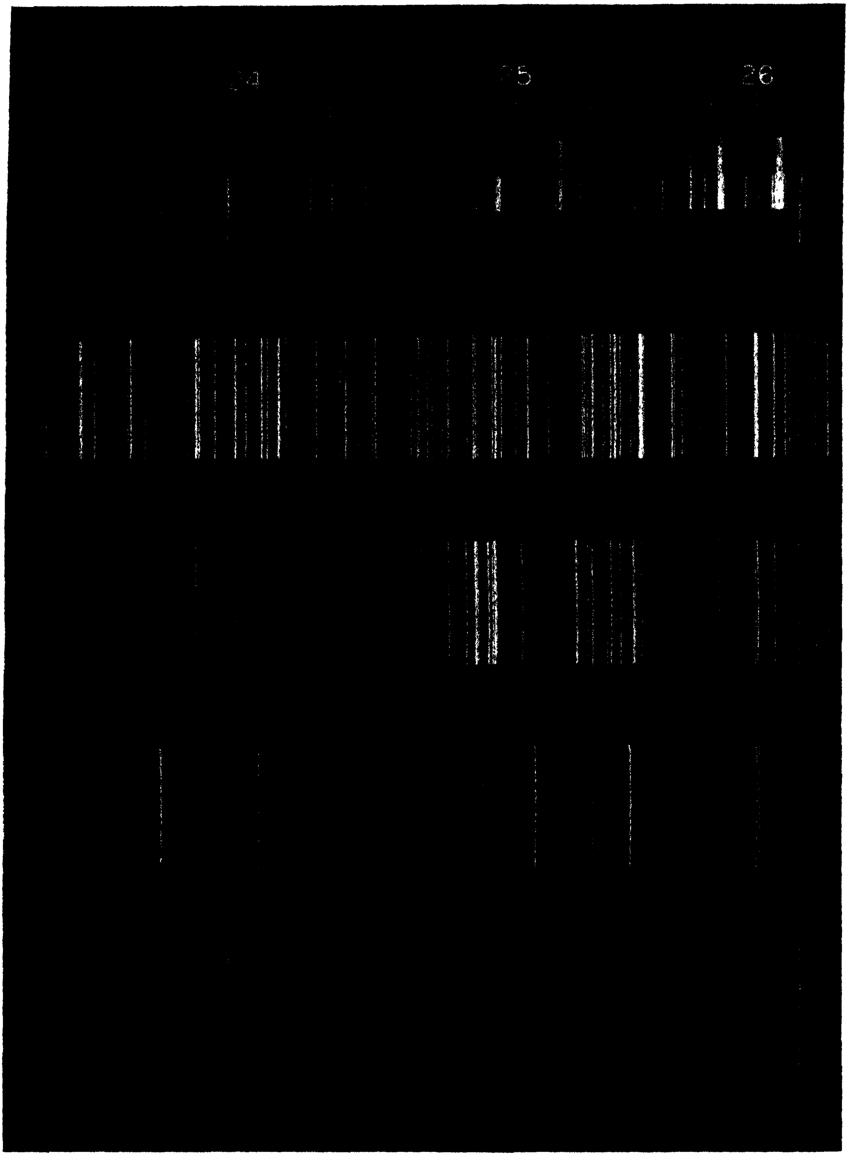

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THE
SPECTROCHEMICAL ANALYSIS OF METALS AND ALLOYS

BY

F. TWYMAN, F.R.S.,
MANAGING DIRECTOR,
ADAM HILGER, LTD.

With Frontispiece, 61 Illustrations in the Text,
and 22 Tables.

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PREFACE.

In writing this book I have had three classes of readers chiefly in mind:

(*a*) Teachers and students of metallurgy who wish to acquaint themselves with the scope and nature of spectrochemical analysis as it is carried out in industrial laboratories.

(*b*) Metallurgists already engaged in industry to whom it may fall to introduce the method for routine control or research.

(*c*) Those who are already engaged in this kind of analysis.

The book is divided into sections commencing with numbers in heavy type, and references from one part of the text to another are made not by pages, but by these numbers. References to the bibliography (which serves also as an author index) are made thus: (Brown, 1936); or where the author's name has been mentioned just previously, thus: (1936).

Sections 160. 1 to 160. 5 are rather out of place at the end of Chapter VIII, and the reader will find them more logically read at the end of Chapter VII.

My interest in the subject dates back to 1898, and arises out of my association since that time with the firm of Adam Hilger, Limited; that interest has indeed been one of the main directive forces in the development of that company during the last forty years. I have endeavoured to avoid particular reference to the firm or its products.

A complete expression of the debt I owe to others is impossible. Among those now dead to whom I owed much for personal interest and encouragement in my early work on apparatus for spectrochemical analysis are the late Lord Rayleigh, G. G. Stokes, H. Kayser, A. de Gramont, W. N. Hartley, and Herbert Jackson. F. Paschen, most helpful to me as to everyone, is, I hope, still alive—when I last heard news of him in 1938 and asked how he passed his time, I was told that his wife said " Immer so ! ", imitating the action of one scanning a spectrogram. Of the great number of living workers in this field, American, Belgian, British, French, German, Italian, Japanese, Swedish, and others, I can say that I do not remember ever to have failed to receive from any one of them any information or help that I have asked for—and I have asked for very much.

A few only will be mentioned to whom I must make acknowledgment for very direct and considerable assistance in preparing this book :

Mr. A. C. Candler has kindly revised the chapter on "The Elements of Atomic Spectrum Theory" which he contributed to *Spectrochemical Analysis in 1938*, and it appears here as Chapter II.

Mr. E. S. Dreblow, chief of the instrument-testing department of Adam Hilger, Ltd., has been of the greatest assistance in every section concerned with practical analysis. His knowledge of handling spectrographs is equalled by few, and if to this is added his practical experience of the various techniques of spectrochemical analysis, the combination must, I think, be one of unique competence. Mr. van Someren's wide knowledge of the literature of the subject has made his reading of some of the proofs very helpful. Mr. D. M. Smith, chief spectroscopist of the British Non-ferrous Metals Research Association, Dr. A. H. Lewis of the Jealott's Hill Research Station, Dr. J. Phelps of the Royal Mint, to whom § 184 is due, and others have corrected or written passages coming within the spheres of their special knowledge ; while the sections on gases (Chapter X), written by Mr. B. S. Cooper of the General Electric Company's Research Laboratory (England), are of special value, dealing as they do with a field so far little exploited in metallurgy.

I ought to add that the appointment by Dr. Hutton of Mr. D. M. Smith in 1927 to the post referred to *above*, and the continued interest in his work of Dr. H. W. Brownsdon, until recently chairman of the Spectroscopic Committee of the Association, constituted one of the most important of the causes of the method coming into such extensive use in this country during the last ten years.

Finally, I would like to mention Dr. Judd Lewis, who has used spectrochemical analysis since 1912 in his work as a consulting chemist. The great bulk of his most important work on the subject has been buried—as far as public recognition goes—in the confidential reports to his clients; but through close touch with him during the whole of that time I can say with confidence that by silent filtration through them it has had a widespread educational effect throughout this country.

Just a word about the title of the book:

When the German "Spektralanalyse" was put into English as "spectrum analysis," the seed was sown of a possible ambiguity of meaning. The phrase might connote either analysis *by means of* the spectrum, or an analysis *of* the spectrum. When physicists became interested in studying the regularities which underly the apparently haphazard distribution of spectral lines, the ambiguity became actual, and those of us who continued to use the phrase in the older sense were thought by some to do so as a result of ignorance.

I succumbed at the suggestion of a friend to the clumsy "spectrochemical analysis." In the writing of this book I have sometimes regretted this, and have glanced with more than half seriousness at such monstrosities as "spalysis" and simplifications like "S.A."

I look with confidence to my friends in the United States to help us out with their genius for coining labour-saving words; till then, when I cannot by circumlocution avoid mentioning what I am talking about, "spectrochemical analysis" must serve.

F. TWYMAN.

January, 1941.

TABLE OF CONTENTS.

PART I.

CHAPTER PAGE

I. THE HISTORY OF THE DEVELOPMENT OF SPECTROCHEMICAL ANALYSIS, FROM NEWTON TO HARTLEY AND DE GRAMONT 1

II. THE ELEMENTS OF ATOMIC SPECTRUM THEORY 42

III. SPECTROGRAPHS AND ACCESSORY APPARATUS 65

IV. THE MICROPHOTOMETER 85

PART II.

V. METHODS OF EXCITING EMISSION SPECTRA 106

VI. TAKING SPECTROGRAMS, MEASURING WAVELENGTHS, AND IDENTIFYING ELEMENTS: BOOKS AND TABLES 146

VII. TECHNIQUES OF SPECTROCHEMICAL ANALYSIS 159

VIII. TYPES OF PROBLEM TO WHICH SPECTROCHEMICAL ANALYSIS IS APPLICABLE 193

IX. THE PRACTICE OF SPECTROCHEMICAL ANALYSIS OF METALS AND ALLOYS:

- Introduction 214
- Aluminium and its Alloys 221
- Cadmium 239
- Copper and its Alloys 241
- Gold 249
- Iron, Steel, and Ferrous Alloys 257
- Lead and its Alloys 278
- Magnesium and its Alloys 286
- Nickel 290
- The Platinum Metals 293
- Radium 296
- Silver 297
- Tin 297
- Zinc and Zinc-base Alloys 297

X. THE ANALYSIS OF SUBSTANCES NOT IN METALLIC FORM, INCLUDING GASES 312

APPENDIX I. Units and Definitions 324

APPENDIX II. Additional Notes 326

BIBLIOGRAPHY AND AUTHOR INDEX 330

SUBJECT INDEX 349

THE
SPECTROCHEMICAL ANALYSIS OF METALS AND ALLOYS.

PART I.

CHAPTER I.

THE HISTORY OF THE DEVELOPMENT OF SPECTROCHEMICAL ANALYSIS, FROM NEWTON TO HARTLEY AND DE GRAMONT.

§ 1. In writing this chapter Kayser's *Handbuch der Spectroscopie* has been my guide. The more I have sought to find material which has escaped his notice, the more impressed I have been with the thoroughness of his historical survey ; and the hours I have spent consulting the works to which he refers have not yielded very much of interest that he has not mentioned (Kayser, 1900).

§ 2. 1672 : Discovery of the Dispersion of Light (Newton).—This discovery was made by the simplest of apparatus. A narrow beam of sunlight coming through a small hole in the shutter of a darkened room was allowed to pass through a prism on to a screen, on which it then formed a strip varying in colour from one end to the other. Newton distinguished seven colours : red, orange, yellow, green, indigo, blue and violet.

Later, with the aid of a second prism, he satisfied himself that these colours were not produced by the prism, for if one of them were isolated and allowed to pass through the second prism no change of colour was produced ; while by a suitable arrangement of the second prism the whole of the colours could be made to overlap on the screen, when by their combination the original white was produced.

One of his arrangements, as depicted in the reference, is shown in Fig. 1. *XY* represents the sun, *MN* is the paper upon which the spectrum of the sun is cast, and *PT* is the image itself. *YKHP* and *XLIT* are two rays, the first of which comes from the lower part of the sun to the higher part of the image, or spectrum, and is refracted in the prism at *K* and *H* ; while the second comes from the higher part of the sun to the lower part of the image, and is refracted at *L* and *I*.

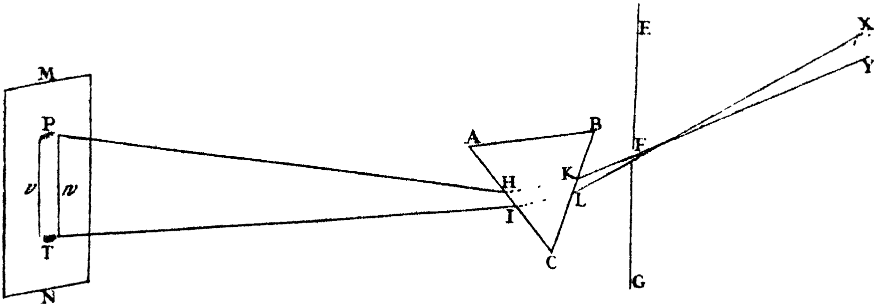

Fig. 1.

What Newton actually effected by these experiments is well summarized in his own words (Newton, 1704) :

> " Part I, Prop. I. Lights which differ in Colour, differ also in degrees of Refrangibility.
>
> " Part I, Prop. II. The Light of the Sun consists of Rays differently refrangible.
>
> " Part I, Prop. IV. To separate from one another the Heterogeneous Rays of Compound Light.
>
> " Part II, Prop. II. All homogeneal light has its proper colour answering to its degree of refrangibility, and that colour cannot be changed by reflexions and refractions.
>
> " Part II, Prop. V. Whiteness and all grey colours between white and black, may be compounded of colours and the whiteness of the Sun's Light is compounded of all the primary Colours mixed in a due proportion."

§ 3. 1800 : Discovery of the Infra-red Spectrum (William Herschel).—William Herschel's contribution (1800*a*) was a striking one. He had noticed that, in viewing the sun through various combinations of differently coloured glasses, with some he felt a sensation of heat though he had but little light, while others gave much light but scarcely any sensation of heat.

This suggested to him that the various rays of the spectrum might have different powers of heating bodies, and he found on trial that it was so. Placing a sensitive thermometer with blackened bulb in various parts of a spectrum from the sun, and observing the change of temperature as compared with that shown by a similar thermometer placed in the shadow, he found differences of 7° in the red but only 3½° in the green,* although the brightness of the spectrum was greatest in the yellow and green, while in the violet the difference was only 2°. More surprising still, in a later experiment (1800*b*) he found that when the thermometer was placed well beyond the red end of the spectrum it showed a temperature of 9°.

§ 4. 1801 : Discovery of the Ultra-violet Spectrum (Ritter).— Ritter's discovery, published a year later than Herschel's, was very directly a step towards spectrochemical analysis as carried out to-day (Ritter, 1801). It revealed the ultra-violet spectrum, in which are found many of the most distinctive lines of the metals, and laid the foundation of photography of the spectrum. His first announcement runs:

" Am 22sten Febr. habe ich auch auf der Seite des Violetts im Farbenspectrum, ausserhalb desselben, Sonnenstrahlen angetroffen, und zwar durch Hornsilber aufgefunden. Sie reduciren noch stärker, als das violette Licht selbst, und das Feld dieser Strahlen ist sehr gross. (Vergl. Annal., 1801, VII, 149. Nächstens mehr davon) ". That is:

" On Feb. 22nd I discovered solar rays at the violet end of the colour spectrum, beyond the same, finding them by means of silver chloride. They reduce more strongly than the violet light itself, and their extent is very great. ([*Cf.* W. Herschel, 1801]. More on the subject later.) "

The reference given by Ritter is to an earlier communication in *Gilbert's Annalen*, in which Herschel, in a résumé of the Royal Society papers already cited, draws attention to an experiment of Scheele's of putting in the visible spectrum a piece of paper coated with silver chloride, which was thereby blackened.

§ 5. 1802 : Explanation of Formation of Spectra by Diffraction Gratings, and First Calculation of Wavelengths (Young).—Thomas Young, at the time the most considerable supporter of the wave

---

* It is not stated in Herschel's paper in what scale the thermometers were divided.

theory of light, deduced from that theory the interference of light, of which the diffraction grating provided him with an illustration (1802*a*).

Young's paper, read before the Royal Society on November 12th, 1801, commenced with an endeavour to show that Newton's opinion with regard to the nature of light differed less from the undulatory theory than was generally supposed, and that a variety of arguments had been advanced against Newton, which might be found considered by Newton himself in a similar form in his own works. Young set forth the wave theory as conceived by himself at considerable length, reinforcing his argument by determining from it the colours of thin plates which had been observed by Newton. He used a grating of 500 lines to the inch, and found that it transmitted red light in four different directions, in accordance with his theory. Young said: "The best subjects for the experiment are Mr. Coventry's exquisite micrometers. Such of them as consist of parallel lines drawn at the distance of one-five-hundredth of an inch are the most convenient." He was able to calculate from the known dimensions of his grating the wavelengths of the colours of the spectrum as named by Newton, as follows:

Red	Orange	Yellow	Green	Blue	Indigo	Violet
650	609	576	536	498	470	442

(The measurements have been converted into millionths of a millimetre.)

In a later paper (1802*b*) he employed the wave theory to explain the colours produced when fibres were held in front of the eye. He found that the brilliancy of the halos surrounding a distant candle, when a lock of wool was held near the eye, was greater the more uniform the dimensions of the fibres.

The diffraction grating provided the means of measuring radiations in wavelengths which is in use to-day.

§ 6. 1802: First Observation of the Dark Lines in the Solar Spectrum (Wollaston).—The sun spectrum as observed by Newton and by other observers up to the time of Wollaston was regarded as a continuous one. Wollaston in 1802 found, however, that it was not so. He says (1802): "If a beam of daylight be admitted into a dark room by a crevice one-twentieth of an inch broad, and received by the eye at a distance of 10 to 12 feet, through a prism of flint glass free from veins, held near to the eye, the beam is seen to be separated into the four following colours only, red, yellowish green, blue and violet . . . The limit of green and blue is not so clearly marked as the rest ; and there are also, on each side of this limit, other distinct dark lines." This was the first description of the Fraunhofer lines.

That they became perceptible, even so imperfectly, is due to the fact that Wollaston restricted the aperture through which the light entered the dark room to a narrow crevice—the forerunner of the spectroscope slit. Wollaston does not seem to have attached much importance to them, nor to the discontinuous spectrum which he noticed on observing in a similar way the light from a candle flame. About the latter he says : " When a very narrow line of the blue light at the lower part of the flame is examined alone, in the same manner, through a prism, the spectrum instead of appearing a series of lights of different hues contiguous, may be seen divided into five images at a distance from each other. The first is broad red, terminated by a bright line of yellow . . . It is, however, needless to describe minutely appearances which vary according to the brilliancy of the light, and which I cannot undertake to explain." The yellow line was, of course, due to the ubiquitous sodium. Young verified Wollaston's observation, although he interpreted it wrongly. He supposed that fine drops of water vapour were converted in the flame into a thin sheet which displayed the interference phenomena of thin sheets. He did not attribute to this cause the bright yellow line (which he also observed)—indeed he could not, since it was doubtless too sharply defined to be so explained.

§ 7. 1817 : Construction of the First Spectroscope and its Use for the First Observation of Metallic Emission Lines (the Yellow Doublet of Sodium). First Measurement of the Lines of the Solar Spectrum, and First Observations of the Spectrum of a Star. Measurement of the Refractive Indices of Various Glasses for the Principal Lines of the Solar Spectrum. First Observation of the Spectrum of the Electric Spark (Fraunhofer).—Perhaps no single paper in the whole history of the subject records so great an advance on the instrumental side as that in which Fraunhofer communicates the above discoveries.

His investigation dealt first with determining the refractive indices and dispersion of various glasses, which he wished to know in order that he might compute the lenses of achromatic object-glasses. The means previously used were not exact enough for this purpose.

Seeking some more definite way of distinguishing the different parts of the spectrum than by their colours, he first tried whether coloured glasses or fluids could be found each of which would transmit light of one colour only. He could find none such ; all he could say was that the colour which distinguished the appearance of each glass or fluid was the most vivid in the spectrum of light which passed through it.

He then tried coloured flames produced by burning alcohol with sulphur, etc., but these also gave no simple light as seen through the prism. He did find, however, in these and all other flames which he tried, one bright, sharply defined line, always in the same place. Some success he achieved by an ingenious contrivance, which is shown in Fig. 2 A row of lamps, *BC*, any of which could be lighted at will, sent light through a dispersing prism *A*, immediately behind which was a narrow slit. The light going through the slit was thus dispersed, so that by lighting one or other of the lamps he could select at will what part of the spectrum should illuminate the second prism. The spectrum or parts of the spectrum were observed by a theodolite *H*, and the deviation of any part measured by means of the divided circle, the refractive index of the prism for each colour being calculated from this deviation.

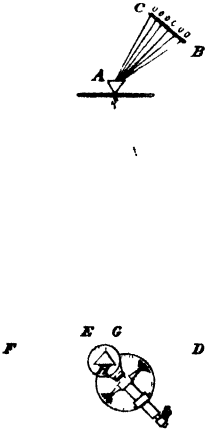

Fig. 2.

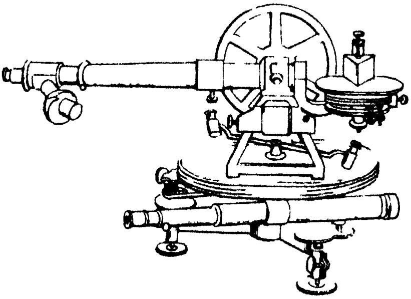

Fig. 2A.

The slit, prism and theodolite constituted the first assembly that could be called a spectroscope. The results obtained were not precise enough, so Fraunhofer set himself to make his apparatus suitable for utilizing sunlight in the same way as he had the light of the several lamps in the row referred to, namely to provide light of various precisely defined colours, by which he could measure the refractive indices of any given glass for a number of colours. He also had in mind to see whether the refractive medium reacted in the same way on sunlight as on artificial light. He soon made a discovery that made the apparatus superfluous for the purpose for which it was intended.

He placed in a darkened room a flint-glass prism immediately in front of his theodolite (Fig. 2A), and let sunlight fall on it through a small slit 24 feet away from the prism. The slit subtended an angle of 15 seconds at the object-glass, not more than about three times what is customarily used in the spectrochemical analysis of metals to-day. He observed the spectrum with the telescope of the theodolite, and saw that the horizontal spectrum was crossed by a great number of dark vertical lines of varying degrees of darkness, some being almost black.

The more important of these lines he distinguished by letters, as shown in the reproduction of his illustration (Fig. 3), and these letters were in frequent use for at least a century thereafter ; indeed they are in no way obsolete even now. How careful his observations were, and what a great step forward had been made by his piece of apparatus, are shown by this figure and by such details as he gives in the text, *e.g.*: "Between D and E, I counted about 84 lines of various strengths. The line D consisted of two strong dark lines close together." (*Translation*). He satisfied himself by many experiments that these lines lay in the nature of the sunlight itself, and were not introduced by the apparatus. He found, too, that if he illuminated the slit with a lamp no such dark lines were visible, but only a bright line exactly in the place of the dark line indicated by D in the solar spectrum.

He had thus succeeded in his plan of producing an apparatus completely satisfactory as regards distinguishing and defining various points of the spectrum.

As he points out, the surfaces of the prism must be very flat and the glass itself free from striæ. He says: "With English flint glass that is never entirely free from striæ, one can only see the stronger lines . . . If one does not possess a prism of satisfactory flint glass, it is best to use a strongly dispersing fluid, for example aniseed oil, but in that case the prismatic vessel must have walls which are very plane and parallel." *

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* Over forty years' experience in testing French, German, and English optical glass, including very recent and careful comparisons, enables me to say that modern English optical glass is in no way inferior to the best of the others.

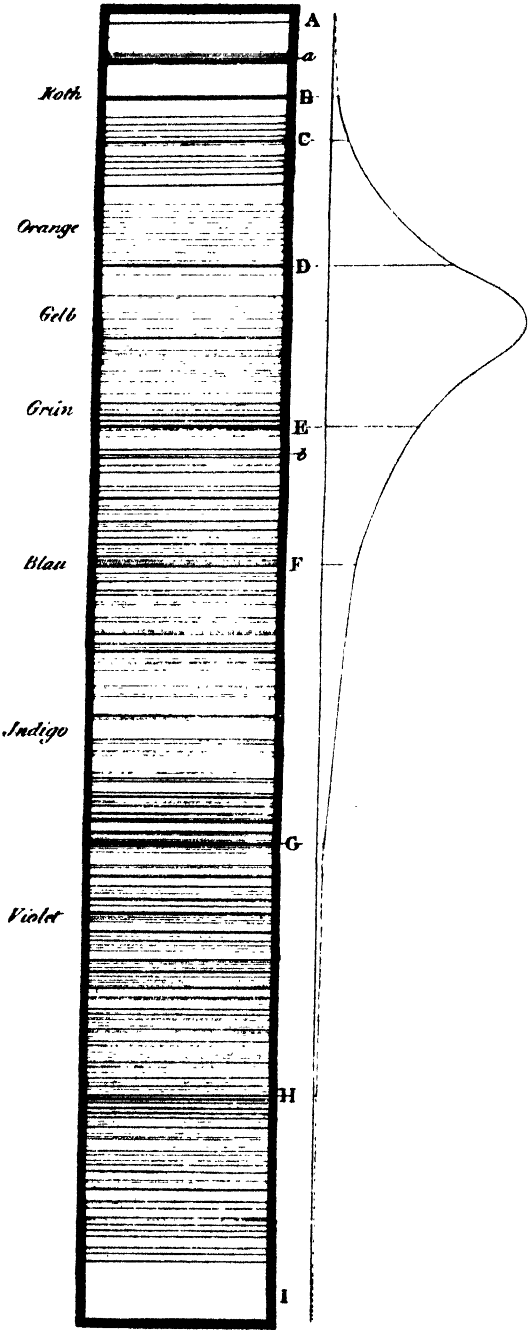


Fig. 3.—Solar Spectrum reproduced from Fraunhofer (1817).

He gives a table of refractive indices of several flint and crown glasses, water and other liquids, and the results enabled him to make achromatic objectives far superior to anything which had been made before ; not only were they corrected for chromatic aberration, but for spherical aberration also.

This paper also describes further experiments with sunlight, light from the stars, flames and the electric spark. He found that Venus showed a spectrum like that of the sun. It was much weaker, but he was able to distinguish the lines D, E, b, and F. Light from the fixed stars was much weaker even than that from Venus, but he was able to see that the light from Sirius showed three broad bands which were quite unlike the sun spectrum.

With electric light he got spectra quite different from those either of the sun or of flames, showing a number of very bright lines particularly brilliant in the green. He concludes: "In all my experiments I could only permit myself, on account of pressure of time, to consider what seemed to refer to practical optics and either to leave other considerations entirely on one side or not to pursue them very far . . . it is therefore much to be desired that those skilled in scientific research should give it their attention." (*Translation*).

Fraunhofer was a practical glass-worker connected with the Utzscheider Optical Institute at Benedictbeuern, near Munich, of which he was the manager from 1818. This connection no doubt gave him access to the theodolite, which turned his apparatus into a real spectrometer. Although he used no collimating lens, and his slit was a wide one, it was a long way from the prism, so that the absence of a collimator and the width of the slit were no great disadvantages. There is good reason for thinking that the definition he obtained may have been not very inferior to that given by a good modern spectrometer of the same dispersion.

In a later paper Fraunhofer (1821) describes his diffraction grating. The phenomenon of diffraction (or, as he called it, "infraction") of light by a grating had, as we have seen, already been observed by Young, but Fraunhofer's gratings, which he made himself, were far more perfect. In a third publication observations with these gratings were continued. He observed the spectra of the electric spark and of the flame without noting anything new of importance.

In observations on the stars he used a telescope of about 4 inches aperture with a prism in front of it, and described a number of spectra so seen.

In a fourth publication (1824) he again examined the spectra of the electric spark.

Fraunhofer in these investigations put forward no hypothesis of the origin of the bright and dark lines in spectra, but he showed how to measure their positions very accurately by the diffraction grating.

§ 8. 1823: An Improved Way of producing the Yellow Line (Herschel).—J. F. W. Herschel, the son of the discoverer of infra-red radiation, gives an account of the absorption of various parts of the solar spectrum by coloured glasses, in the course of experiments made in search of a homogeneous flame for illuminating microscopic objects. He found, like Fraunhofer before him, that he was unable to get in this way the purity of light that he wanted. It is true that he was able to get fairly homogeneous red light by using a sufficient thickness of one of his glasses, yet the quantity of light extinguished was so great as to render what remained of little use.

Had it been possible to isolate the most luminous rays of the spectrum as perfectly as the extreme red, the advantage, he said, would then have been very considerable, but after many trials he came to the conclusion that the separation of homogeneous green or yellow light of any considerable intensity could not be effected by any coloured media then known. The position is much the same to-day as far as coloured glasses are concerned, but we now have means of obtaining monochromatic light-sources of great brightness, such as the mercury, sodium and other vapour lamps, used with or without filters.

Investigating the yellow light produced by placing common salt or nitre in the flame of burning alcohol, Herschel noticed that almost all bodies " in which the combustion was imperfect " gave a light in which these homogeneous yellow rays predominated, and he eventually found a way of producing a flame emitting abundant yellow homogeneous light. He obtained this by putting a wire gauze about half an inch above the wick of a spirit lamp, the gauze being moistened by contact with a sponge as soon as it had been made red hot, and he found that the flame obtained in this way without deliberate introduction of a salt of sodium was more satisfactory than one into which he had deliberately put such salt, one of the objections to the use of which was the " insalubrious vapours disengaged during the combustion of these salts." He was under the impression that the yellow rays, now known to be due to sodium, were the product of imperfect combustion (1823). He tinged a flame with a solution of " muriate of strontia," and viewing it through a prism " with the usual precautions to diminish the angular breadth of the incident pencil " saw a broad but well-defined red and a narrow yellow image. He examined also flames coloured with a number of other salts; but his interest throughout was in the colour of the flame, and he does not seem ever to have thought of the spectrum as a means of detecting the substance which causes it.

1840: Photography of Absorption Spectra (J. F. W. Herschel).—In a second paper (1840) Herschel describes many experiments on the effect of the different rays of the solar spectrum on a variety of chemical substances, using a number of photographic processes. In the course of this work he took photographs of the solar spectrum, some of them through coloured glasses and other coloured media. On this subject he makes an observation which deserves quoting:

" To study this subject in its most simple form, it would be necessary to operate on some preparation which shall be equally and indifferently sensitive to every ray of the spectrum. Such a preparation, with exception of the rays beyond the extreme red, exists in the bromuretted paper of Art. 77. But when the paper used to receive the spectrum, after undergoing absorptive analysis, has its own peculiar law of sensitiveness, it is evident that the resulting impression left on such paper will be a mixed effect, depending on two distinct functions, the one expressing the degree of transmissibility or *diacratic* index of the medium for that ray, the other that of sensibility in the paper to the action of such ray."

His spectrograph took several slightly different forms, of which the following is one: A clock-driven polar axis carried a flint prism by Fraunhofer. The apparatus being kept in the same orientation relative to the sun by the clockwork, the beam of sunlight falling on the prism was received by an achromatic lens of 26 inches focal length, which formed the solar spectrum at its focus. Nothing corresponding to a slit was used in this group of experiments, but a passage in his earlier paper shows that he knew of it and used it on occasion.

§ 9. 1826: Observation of the Lines of Sodium, Potassium, and Strontium (Talbot).—In this paper (1826) W. H. Fox Talbot comes very close to discovering Spectrochemical Analysis.

His paper is entitled " Some Experiments on Coloured Flames." He employed for his flames a cotton wick, which he soaked in a solution of the salt whose spectrum he wished to observe, dried, and used in a spirit lamp. His spectroscope was very simple, but very effective. The flame was put behind a screen having a narrow vertical slit, through which the flame could be seen. This slit so illuminated and examined with a prism gave the spectrum of the flame. He appears to have been the first to obtain a flame which did not show the yellow sodium line. He says : " If a clean piece of platina foil is held in the blue or lower part of a gas flame, it produces no change in the flame, but if the platina has been touched by the hand it gives off a yellow light which lasts for a minute or more."

Speaking of a red ray observed with the flame of nitre or of chlorate of potash, Talbot says : " This red ray appears to possess a definite refrangibility and to be characteristic of the salts of potash, as the yellow ray is of the salts of soda . . . If this should be admitted I would further suggest that whenever the prism shows a *homogeneous* ray of any colour to exist in a flame, this ray indicates the formation or the presence of a definite chemical compound."

Finally, he found that the red fire used in theatres, examined in the same way, gave a most beautiful spectrum with many bright lines or maxima of light, and in respect of these he concludes : " For instance, the orange ray may be an effect of strontia, since Mr. Herschel found in the flame of muriate of strontia a ray of that colour. If this opinion should be correct and applicable to the other definite rays, a glance at the prismatic spectrum of a flame may show it to contain substances which it would otherwise necessitate a laborious chemical analysis to detect."

§ 10. 1832 : Experiments leading to the Conclusion that the Original Light from the Sun forms a Continuous Spectrum, and that the Dark Fraunhofer Lines are Due to the Vapours surrounding the Sun (Brewster).—The above conclusion was announced by Brewster in a report on " The Recent Progress of Optics " at the second meeting of the British Association (Brewster, 1832). He says : " For reasons which I may have an opportunity of explaining in another communication, I conceive that the original light of the sun is continuous from one end of the visible spectrum to the other and that the deficient rays are absorbed by the gases generated during the combustion by which the light is produced." The account of the experiments which led to this conclusion was duly published (1834), although strangely enough he does not in his 1834 paper reaffirm the statement just quoted.

Brewster was studying the solar spectrum with the principal object of finding a general principle of chemical analysis in which bodies might be characterized by their *absorption* of definite parts of the spectrum. When he used nitrous acid gas as the coloured medium, using the light of a lamp, he was surprised to observe the spectrum crossed with hundreds of lines or bands, "far more distinct," he says, "than those of the solar spectrum." Of this experiment he says: "The result of this experiment . . . presented me with a phenomenon so extraordinary in its aspect—bearing so strongly on the rival theories of light—extending so widely the resources of the practical optician, and lying so close to the root of atomical science, that I am persuaded it will open up a field of research which will exhaust the labours of philosophers for centuries to come."

It must be remembered that no absorption *lines* had been observed before from any terrestrial source.

§ 11. 1834: The Spectra of Lithia and Strontia (Talbot).—In an account of a number of brief, unconnected "Facts relating to Optical Science" Talbot (1834) includes the following very clear statement:

"*On the Flame of Lithia.*

"Lithia and strontia are two bodies characterised by the fine red tint which they communicate to flame. The former of these is very rare, and I was indebted to my friend Mr. Faraday for the specimen which I subjected to prismatic analysis. Now it is difficult to distinguish the lithia red from the strontia red by the unassisted eye. But the prism displays between them the most marked distinction that can be imagined. The strontia flame exhibits a great number of red rays well separated from each other by dark intervals, not to mention an orange and a very definite bright blue ray. The lithia exhibits one single red ray. Hence I hesitate not to say that optical analysis can distinguish the minutest portions of these two substances from each other with as much certainty, if not more, than any other known method."

This statement clearly establishes Talbot's right to be regarded as the discoverer of spectrochemical analysis.

§ 12. 1835: The Nature of the Continuous Spectrum (Talbot).—In this paper Talbot draws attention to the well-known fact that a piece of lime held in an oxy-hydrogen flame gives a very bright light, and to the opinion generally held at the time that this was due to the production and burning of calcium. He held this opinion to be incorrect, and after describing an experiment to settle the point he says : " In short, we see that the *mere presence* of the lime in a heated state is the cause of the light . . . I am of the opinion, therefore, that the emission of intense light by a particle of lime in this experiment, without the loss of any portion of its own substance, arises from the cause above referred to—namely that the heat throws the molecules of lime into a state of such rapid vibration that they become capable of influencing the surrounding ætherial medium and producing in it the undulations of light."

This is a material step towards understanding the difference between the causations of continuous and of line spectra.

Later on in the same paper he considers what conclusions may be suggested respecting the nature of light from its absorption in the case of the dark line spectrum discovered by Brewster in nitrous and other coloured gases. Referring to the dark lines in the spectrum produced by iodine vapour, Talbot remarks :

" I have found by careful observations that they are not equidistant, but that they become gradually more crowded towards the blue end of the spectrum . . .

" This approximation of the lines takes place gradually, and seems a consequence of some simple general law. Now in the former part of this paper I have advanced the hypothesis that the vibrations of light and those of material molecules are capable of mutually influencing each other. It remains to be seen whether the same hypothesis does not afford a clue to the explanation of this apparently complex phenomenon of absorption.

" It is known that certain gases combine rapidly when exposed to sunshine, which do not unite in the dark : no doubt because the light causes the molecules to vibrate, so as to come within the sphere of each other's attraction.

" I conclude from this, and many other facts of the same kind, that light when traversing a transparent medium is able to excite motion among its particles. This being admitted, let us suppose iodine vapour so constituted that its molecules are disposed to vibrate with a rapidity not altogether dissimilar to that of light. Now, if the different coloured rays differ also (as is probable) in rapidity of vibration, some of them will vibrate *in accordance* and others *in discordance*, with the vibrations of iodine gas, and these accordances will succeed each other in regular order from the red end of the spectrum to the violet end ; "—But here unfortunately he spoils the picture somewhat by continuing :—" each discordance being marked by a dark line or deficiency in the spectrum, because the corresponding ray is not able to vibrate through the medium but is arrested by it and absorbed." Compare the remark of Stokes quoted in § 26. 1 : it is the *accord*, not the *discord*, between the vibrations of light and the possible states of atoms or molecules that causes absorption by the latter.

§ 13. 1836 : The Spectrum of Silver, Gold, and Copper (Talbot).— Later (1836), in a further collection of " Facts relating to Optical Science," Talbot says : " It is much to be desired that an extensive course of experiments should be made on the spectra of chemical flames, accompanied with accurate measurements of the relative position of the bright and dark lines, or maxima and minima of light which are generally seen in them. The definite rays emitted by certain substances, for example the yellow rays of the salts of soda, possess a fixed and invariable character which is analogous in some measure to the fixed proportions in which all bodies combine, according to the atomic theory." He adds : " Silver-leaf deflagrated by galvanism gave a spectrum with several definite rays, among which two green rays appeared to me to possess nearly the same tint, although differing in refrangibility.

" Gold-leaf and copper-leaf each afforded a fine spectrum exhibiting peculiar definite rays. The effect of zinc was still more interesting ; I observed in this instance a strong red ray, three blue rays, besides several more of other colours. These experiments were made in the laboratory of the Royal Institution in June, 1834."

William Henry Fox Talbot is the Fox Talbot whose name will be familiar to everyone since the centenary of his production of the earliest recorded photograph on paper in 1834.

I cannot refrain from quoting from the *Dictionary of National Biography* a short passage illustrating his remarkable versatility :

" Talbot's name is so closely associated with the beginnings of photography that his mathematical powers have been overshadowed. In his memoir " Researches in the Integral Calculus " published in the *Philosophical Transactions* (1836, pp. 177-215 and 1837, pp. 1-18) he gave an account of his investigations upon the comparison of transcendents, which shows that he had independently been led to consider the development and generalisation of Fagnani's theorem, and was on the track that might have led him to rediscover Abel's great theorem. In 1842 he read at the British Association (Report, pp. 16-17), a paper " On the Improvement of the Telescope," and in the 41st report (1871, pp. 34-36) there is a paper " On a New Method of Estimating the Distance of some of the Fixed Stars." He was, with Sir Henry Rawlinson and Dr. Hincks, one of the first to decipher the cuneiform inscriptions brought from Nineveh, and he made numerous contributions in literature and archæology to the Royal Society of Literature and to the Society of Biblical Archæology.

" He was elected a member of the Royal Astronomical Society on 13th December, 1822, and a Fellow of the Royal Society on the 17th March, 1831, receiving the Royal Medal in 1838 and the Rumford Medal in 1842. He sat in the first reformed parliament for Chippenham from 1833 to 1834, and then retired from politics. He died at Lacock Abbey on 17th September, 1877, having married on 20th December, 1832, Constance, youngest daughter of Francis Mundy of Markeaton, Derbyshire.

" Of his writings the most interesting is ' The Pencil of Nature ' which was issued in six parts in 1844-6. It is the first book ever illustrated by photographs produced without any aid from the artist's pencil ; it is now very rare. His other works were :—

1. ' Legendary Tales, in verse and prose,' collected 1830.
2. ' Hermes, or Classical and Antiquarian Researches,' 1838-9, two numbers only.
3. ' The Antiquity of the Book of Genesis,' 1839.
4. ' English Etymologies,' 1847.
5. ' Assyrian Texts Translated,' 1856.

He also contributed an appendix to the second edition of the English translation of G. Tissandier's ' History and Handbook of Photography,' 1878, and in the catalogue of scientific papers he is credited with fifty-nine contributions.

" A portrait of Talbot is in the South Kensington Museum in the collection of ' Fathers of Photography '."

§ 14. 1835 : Drawings of the Spark Spectra of Sodium, Mercury, Zinc, Cadmium, Bismuth, Tin, and Lead (Wheatstone).—In a very brief notice of a communication made by Wheatstone (1835) at the 1835 meeting of the British Association, his observations are described as follows :

" 1. The spectrum of the electro-magnetic spark taken from Mercury consists of seven definite rays only, separated by dark intervals from each other ; . . . The observations were made with a telescope furnished with a measuring apparatus ; . . . 2. The spark taken in the same manner from Zinc, Cadmium, Tin. Bismuth and Lead in the melted states, gives similar results ;

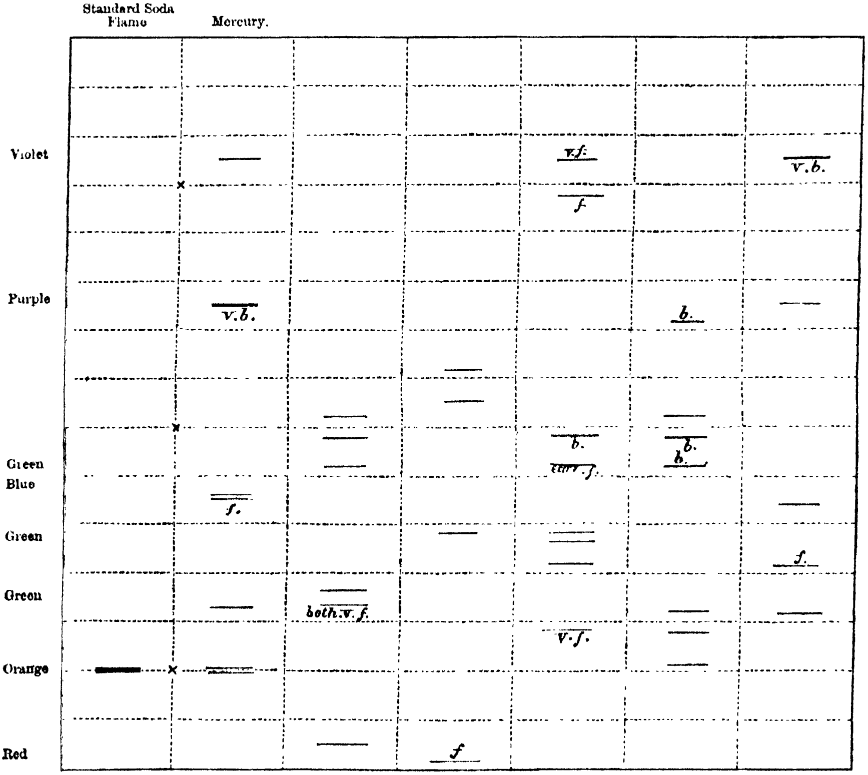
but the number, position and colours of the lines varies in each case; the appearances are so different, that, by this mode of examination, the metals may be readily distinguished from each other. A table accompanied the paper, showing the position and colour of the lines in the various metals used. . . . 3. When the spark of a voltaic pile is taken from the same metals still in the melted state, precisely the same appearances are presented. . . . Professor Wheatstone also examined, by the prism, the light which accompanies the ordinary combustion of the metal in oxygen gas and by other means, and found the appearances totally dissimilar to the above."

Wheatstone's paper was not published, except in the brief abstract from which the above quotation is taken, until twenty-five years later (Wheatstone, 1861). On reference to his later paper we find that the "electro-magnetic spark" was produced by an induction coil with a mechanical interrupter. The paper also includes the table referred to, which is reproduced in Fig 4. Wheatstone's apparatus is in the Science Museum, London, and is similar in principle to Gerlach's interrupted arc.

§ 15. 1840 : The Search for Spectrum Lines in the Ultra-violet (J. F. W. Herschel).—Ritter's discovery of the action of ultra-violet light on silver chloride had no further developments as far as spectroscopy was concerned, until J. F. W. Herschel's paper (1840) on "The Chemical Action of the Rays of the Solar Spectrum on Preparations of Silver and other Substances, both Metallic and Non-metallic, and on some Photographic Processes."

Herschel had tried a number of combinations of light-sensitive substances in the endeavour to increase the sensitiveness of photographic paper, but after all his trials he freely admitted that the specimens prepared by Fox Talbot far surpassed in respect of sensitiveness any that he himself had produced of a manageable kind, and for all ordinary purposes he ended by adopting Talbot's process. Herschel's experiments were directed to the detection of dark spaces in that portion of the spectrum which he called the "chemical," or, as we should say, "actinic," similar to the lines of Wollaston and Fraunhofer in the visible spectrum. He allowed sunlight to pass through a narrow slit, and using paper prepared on Talbot's principle (which he describes on p. 10 of his paper) found a maximum of action in the blue-green region of the spectrum near Fraunhofer's ray F. He also found that the extent of the recorded spectrum beyond the visible violet light far surpassed his expectations, the visible termination of the violet rays being nearly in the middle of the photographic image impressed on the paper. He found that the red part of the spectrum was inactive, and that where the orange-red rays fell the paper assumed a sort of dull brick-red colour. His imagination seems to have been greatly struck by this variation of colour of the photographed image, with which a great part of his paper is concerned. His description of the apparatus, which mentions only a slit and no lens, makes it clear why this experiment was not successful in producing good enough definition to give him any photographed detail of the Fraunhofer lines, and in his further experiments he adopted an optical arrangement still less likely

Table of the Bright Lines in the Spectrum of the Magneto-Electric Spark, taken from different melted Metals, and observed with the Prismatic Telescope.



ABBREVIATIONS :—*b*, bright; *v b*, very bright; *f*, faint; *v f*, very faint.

The above relative measurements were taken by means of a ruled glass micrometer, placed in the focus of the eye-piece of the telescope.

Fig. 4.—Wheatstone's Drawing of Metallic Spark Spectra.

to do so. He used in his later apparatus a highly refractive and dispersive flint-glass prism, which was the personal gift of Fraunhofer, "of faultless purity and perfect workmanship," and he allowed the rays transmitted by the prism to fall on a crown-glass lens which was evidently placed some distance from the prism, since he says that any part of the spectrum might fall on the lens so that at will he could give a great concentration of light at any desired degree of refrangibility, the rays being thrown into long coloured caustics owing doubtless to the excessive aberration of the lens for rays off the axis.

With this he made an interesting observation, namely that when he adjusted his lens to give the best definition for rays beyond the ordinary visible violet but within the limit of the chemical action, the portion of it thus concentrated was apparent to the eye as a greyish-white "insulated" oval spot. This he assumed to be visible light of rays beyond the violet and he described the colour as "lavender grey." One might be inclined, from this description and from the fact that in recent years it has been observed that with a powerful monochromator light can be observed of wavelength 3125A. (Goodeve, 1934) –far beyond what was previously thought to be the limit of visibility—to assume that Herschel had observed the same phenomenon nearly 100 years before. It is not conceivable, however, that light of this wavelength could be visible in a spectrum produced by a flint-glass prism and thrown on to paper. What Herschel observed must have been fluorescence.

A later arrangement in which his apparatus was directed towards the sun and maintained so by clockwork was no more likely, owing to its dimensions and the fact that apparently no slit was used, to give a photograph of the Fraunhofer lines. Where Herschel failed, however, Becquerel succeeded (1842).

§ 16. 1842 : The First Photographs of a Spectrum (the Solar Spectrum) (Becquerel and Draper independently).—Becquerel's investigation was concerned with the effect produced on sensitive substances by the chemical action of different parts of the solar spectrum. The paper also deals with the phosphorescence and the heating effects produced by the different rays. The train of thought into which he was led by his investigations will be realized from a résumé of his conclusions, which were as follows :

"(1) A beam of solar rays is a combination of an infinity of rays of diverse refrangibility, each ray being derived from waves in the ether having the same speed.

"(2) When such a beam of rays is dispersed by a prism, a spectrum is produced, the various parts of which have different action on bodies on which they fall.

"(3) If the rays fall on molecules which are united by feeble affinities only, such as salts of silver, gold, mercury, etc., those rays are active whose speeds of vibration can be transmitted to the molecules of the substance.

"(4) Phosphorescent bodies become luminous as a consequence of molecular movement, a movement which gives place to the separation of the two electricities which maintain the molecular equilibrium, the neutralization of which produces the glow which we observe. The difference between this action and the chemical one is that the mechanical movements of the molecules of the ether are transmitted to the bodies without chemical decomposition.

"(5) If further, one considers the retina as an organ which perceives the vibrations, it is only affected by the rays comprised within certain limits of refrangibility, and these rays form a spectrum therefore, which can be seen." (*Free Translation*).

These conclusions, so closely in accord with modern notions, are only incidental to the fact that Becquerel in his experimental investigation actually took a photograph of the spectrum, showing the Fraunhofer lines and lines of a similar character in the ultra-violet portion of the spectrum. The effect was obtained owing to his happy choice of type of apparatus. He used a slit only 0·25 mm. wide. This was placed 2 metres away from the prism of flint glass, and immediately after this was placed a lens of 1 metre focus, so that the image of the spectrum was formed about 2 metres from the lens. Such an arrangement should give a spectrum, if the optical work were reasonably good, of very great dispersion and good definition. By placing in the focus an iodized silver plate, as invented by Daguerre, exposing it for a minute or two, and developing in mercury vapour, he obtained an image extending from the indigo to beyond the extreme violet, and observed a great quantity of fine lines throughout that region.

§ 17. Draper, Professor of Chemistry at the University of New York, succeeded in getting a photograph of the Fraunhofer lines at about the same time (1842). Having returned to New York from a long journey, he wrote to the *Philosophical Magazine* sending a photograph of the solar spectrum, asking that it should be transmitted to Sir John Herschel. "Obtained as it was in the South of Virginia," he says, "probably you can make nothing like it in England. The sunlight here in New York failed to give any such result." He used the yellow iodide of silver (Daguerre's preparation) and an exposure of 15 minutes. His short letter does not make it quite clear that the spectrum revealed the presence of the Fraunhofer lines. However, in a further communication (1843), he used an apparatus with which he both saw and photographed the Fraunhofer lines. He gives the dimensions of his apparatus, and once again one perceives how inevitably success in detecting Fraunhofer lines was linked up with the dimensions of the apparatus. He used a slit, and as far as I have been able to find, he was the first to use an adjustable one; he refers to "A slit being formed by a pair of parallel knife edges, one of which was movable by a micrometer screw . . . The screw was adjusted so as to give an aperture $\frac{1}{32}$ inch wide and the light passing through fell upon an equi-angular flint glass prism placed at a distance of 11 feet. Immediately on the posterior face of the prism, the ray was received on an achromatic lens, the object glass of a telescope, and was brought to focus at a distance of 6 feet 6 inches, at which place an arrangement was adjusted for exposing white paper screens, on which the more prominent fixed lines might be seen and their position marked, or sensitive plates substituted for the screens, occupying precisely the same position." The lines beyond the visible violet were very numerous. He continues: "If, as it has been said, nearly 600 have been counted between A and H, I should think there must be quite as many between H and P." One must remember that A is in the far red and H not far from the end of the visible violet.

§ 18. 1845: Photographs of Grating Diffraction Spectra (Draper).—In 1845 Draper turned his attention to the spectra produced by gratings, or as he called them "interference spectra." A slit $\frac{1}{30}$ inch wide being used at a distance of 12 feet, the solar light directed on to the slit by a heliostat fell on a piece of flat glass the surface of which was ruled with parallel lines, and this, having been silvered with tin foil and mercury in the manner employed for mirrors, served the purpose of a grating, the reflected beam producing the well-known series of interference spectra. He points out that the angular separations of any two colours from the incident ray are to one another in the proportion of their wavelengths. An image being formed of a spectrum on a ground screen or sensitive surface, the Fraunhofer lines could be seen, and he photographed the spectrum in half an hour on a daguerreotype plate.

§ 19. 1852: Drawings from Visual Observations of the Ultra-violet Solar Spectrum using Glass Prisms (Stokes).—This research was suggested by the discovery by Sir John Herschel of the "superficial colour" (fluorescence) produced in quinine sulphate by light. Its interest for us here lies in Stokes' observation of the Fraunhofer lines in the violet and similar lines in the ultra-violet. The arrangement by which he saw these ultra-violet lines consisted of a slit about $\frac{1}{20}$ inch wide, three or four "Munich" glass prisms placed at a distance of several feet from the slit, and a lens "of rather long focus" placed immediately after the last prism, forming an image of the spectrum in which the quinine sulphate was placed.

With this arrangement he saw a fluorescent strip crossed with dark lines in the violet which he identified with the Fraunhofer lines. Beyond this the fluorescence (or, as he called it, the "dispersed light") became of a dull sky-blue colour, and beyond H a good number of lines were visible. One may consider the visible spectrum formed under such an arrangement as ending at about H, and a plate accompanies the paper in which Stokes gives to the principal broad lines or bands which he saw the designations: k, l, m, n, o, p. His "k" corresponds with the "k" on Professor Draper's map. Stokes' "l" is omitted from Draper's map, but is identified by Stokes with Becquerel's "l." There is no point in dwelling further on the letters given by these investigators to the lines they observed. The point of interest to us now is the observation and the recording by Stokes of these ultra-violet absorption lines in the sun spectrum.

Stokes, in his lengthy paper, gives the results of the effect of various parts of the spectrum on a great number of fluorescent substances. When he wrote this paper Stokes had not seen Becquerel's map of the ultra-violet lines.

§ 20. 1855: Visual Observation of the Ultra-violet Solar Spectrum with a Quartz Spectroscope (Helmholtz).—Helmholtz, investigating the sensitiveness of the eye to the ultra-violet, had found with a glass instrument that the radiation could be seen nearly as far as the p line of Stokes, provided the eye was protected from the remainder of the spectrum. When he had a quartz instrument made he saw the p line itself, which indeed Stokes himself had already done. The ultra-violet light looked when faint deep indigo, when stronger a whitish blue. This showed that he was not merely perceiving the fluorescence of the eye, which is green in colour. The above was the instrument used by Esselbach (§ 23).

§ 21. 1856: Introduction of a Collimating Lens into a Spectroscope, for the Determination of the Refractive Index and Dispersive Power of Various Media (Meyerstein).—Meyerstein in this paper (1856) says that Steinhardt and Seidel have shown that the small use of Fraunhofer's beautiful method (of determining refractive indices) is partly due to an oversight in Fraunhofer's calculation. This author thinks, however, that another reason might be that the adjustment could scarcely be effected without the aid of an assistant.

To avoid the large dimensions of the apparatus he introduced an achromatic objective separated from the slit by its focal length, the "collimating" lens which is now an indispensable part of all prism spectrographs.* The rest of the paper—dealing with the measurement of the angular values of the dark lines in the solar spectrum and of the angle of the prism, so as to determine accurate values of its refractive index and dispersion—need not concern us.

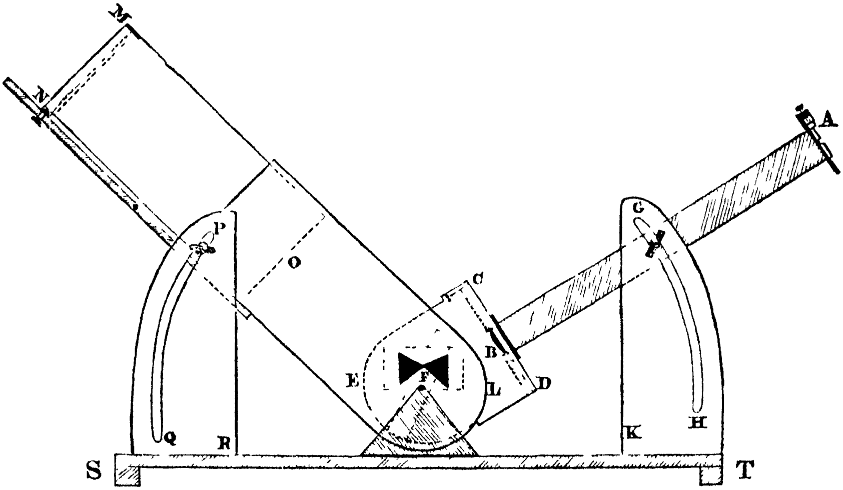


Fig. 5.—Two-prism Quartz Spectrograph (Crookes, 1856).

§ 22. 1856: A Two-prism Quartz Spectrograph (Crookes).—This spectrograph (Fig. 5) had two quartz prisms with faces 1·8 × 1·1 inches, angle 55°, so cut that the rays passed through them along the optical axis—"thus avoiding the ill effects which would be caused by double refraction." One is inclined to think he must have been lucky enough to have one prism of left and one of right rotation quartz, otherwise he would have had quite enough double refraction to duplicate and to spoil the contrast of the Fraunhofer lines. He used one quartz lens, of 12 inches focus, and if, as appears certain from the figure, his photographic plate was about the same distance (or a little more only) from the prisms, he could not have obtained very good definition

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* Although the purpose of the collimator lens is occasionally served by the prism having one or two spherical surfaces.

§ 23. 1856: Measurements of Wavelengths in the Ultra-violet Spectrum (Esselbach).—The measurements described in this paper, like those described in § 19, were made possible by the discovery of fluorescence.

Stokes had shown that when the glass of a spectrum apparatus was replaced by rock crystal, an ultra-violet spectrum then became visible equalling the entire length of the Newton spectrum.

Prof. Helmholtz lent Esselbach his quartz spectrum apparatus and also the work-room in the Physiological Institute at Königsberg. The author directed the sunbeams horizontally into a darkened room in which were two prisms, the one as near to, and the other as far from, the window as space permitted. The first prism spread the beams into a medium spectrum in which each colour was represented by a wide pencil of light. The rays passed on so that at a distance of 2 feet the spectrum consisted of a white portion with coloured ends. If in one of the ends a large screen with a hole therein was put, only a part of the spectrum was utilized in either the most or the least refrangible part. In the telescope the slit was then seen through the prism as a homogeneous spectrum with sharp Fraunhofer lines, in which those colours were particularly noticed in which the slit was favourably illuminated.

The method Esselbach used to determine the wavelengths was based on Talbot's phenomenon, in which a thin plate of transparent substance is placed half way over the object-glass of the telescope on the violet side. The spectrum is then seen regularly divided into bright and dark strips, and from the known optical qualities of the thin plate wavelengths of the maxima can be determined, and hence of the Fraunhofer lines which lie on these maxima.

From his measurements he made a very good drawing of the ultra-violet spectrum, designating the more prominent lines by letters of the alphabet: L, M, N, O, and so forth. It will be noted that his apparatus was very similar to Fraunhofer's, and it probably gave very good definition. It is interesting to give the values of his wavelengths as compared with Fraunhofer's in the visual, from which the accuracy for the ultra-violet may be inferred. The agreement must be considered very good. Rowland's measurements (1895) differ from the most modern ones by from 0·6 to 3·5 in the fifth significant figure.

TABLE I.—CALCULATED AND OBSERVED WAVELENGTHS OF THE FRAUNHOFER LINES.

Lines.	Wavelengths calculated by Esselbach.	Fraunhofer's Measurements.	Rowland's Measurements.
	mm.	mm.	mm.
B	0·0006874	0·0006878	...
C	...	0·0006564	0·0006563 045
D	0·0005886	0·0005888	...
E	0·0005260	0·0005260	...
F	0·0004845	0·0004843	0·0004861 527
G	0·0004287	0·0004291	...
H	...	0·0003929	0·0003968 625
L	0·0003791	...	...
M	0·0003657	...	...
N	0·0003498	...	...
O	0·0003360	...	...
P	0·0003290	...	...
Q	0·0003232	...	...
R	0·0003091	...	...

§ 24. 1858: Spark Spectra of Salts on Metallic Electrodes (Willigen).—Van der Willigen showed that when a solution of a metallic salt was put on metallic electrodes the spark showed the spectrum of the metal of the salt in addition to that of the electrodes. He states more clearly than any predecessor under which conditions the lines of the gases or of the electrodes are dominant. Using as electrodes wires 1 mm. in diameter of various metals, he enclosed them in tubes so that he could surround them with atmospheres of various gases at various pressures.

When the electrodes were widely separated he got the lines of the gases; when they were close together those of the metals. He used an induction coil with a Leyden jar, and found that the lines due to the salts were very bright when the electrodes were moistened with hydrochloric acid.

§ 25. 1860: Photography of the Lines in the Ultra-violet Solar Spectrum (Müller).—J. Müller (1860) used a quartz spectrograph to obtain photographs of the ultra-violet solar spectrum, but the definition given by the instrument was poor. Owing to lack of funds, it was some time before he could procure the heliostat and quartz apparatus, and so he was only able to try in the autumn of 1858 the experiment which he had proposed to himself some time earlier. The quartz prism was cut with the optical axis perpendicular to the edge of the prism and parallel with the third side of the prism. If, however, he used the prism so that the rays passed along the optical axis, he found it was not possible to get a spectrum showing the Fraunhofer lines. He could adjust the apparatus to get one of these lines visible, but then the others were not seen. The reason doubtless was that for all rays except those passing along the axis, quartz is sufficiently doubly refracting to obliterate the Fraunhofer lines. It is also doubly refracting along the axis, although very slightly so.

He then placed the prism so that that surface of the prism with which the optical axis was parallel was one of the refracting surfaces, and in this manner (owing to the strong double refraction of the quartz) he got two spectra, in which, although they somewhat overlapped, yet a considerable portion of each was free from overlapping, so that the Fraunhofer lines from F to H were visible. Forming an image of the spectrum with a quartz lens of 4 ft. focus a photograph was taken by his collaborator, Th. Hase, the spectrum being greatly extended beyond what could be photographed with a glass prism.

Müller ascribed the poor definition to the overlapping of the more refracted spectrum by the ultra-violet part of the less refracted one, and to remove this difficulty introduced an achromatized quartz prism, consisting of two prisms cemented together with Canada balsam as described in his *Lehrbuch der Physik*, 5th edition, **1.** This prism gave two separated beams of light polarized in planes at right angles to each other. By turning the quartz prism the two beams could be made to lie one below the other, and on placing the quartz prism which was to form the spectrum in *one* beam, a single spectrum was formed.

He appreciated the possibility of the layer of Canada balsam absorbing part of the ultra-violet radiation, but was hopeful that being so thin it would have little effect. With this spectrograph Hase took many photographs in the sunny days of July, 1859, of the best among which he says that one of the photographs showed the lines M, N, and O with an exposure of only 2 seconds, whereas the glass spectrograph scarcely extended beyond N with an exposure of 15 seconds.

The extreme line of the visible spectrum named by Fraunhofer was H, and consists of two strong dark strips separated by a space somewhat greater than the width of the strips themselves. Photographed with Müller's glass spectrograph with an exposure of 1 and 2 seconds each of these strips was revealed as a collection of fine dark lines close together, as shown in Fraunhofer's drawing of the spectrum (Fig. 3). He describes the appearance of the groups of ultra-violet lines which Stokes (1852) designated by l, m, n (though Müller writes L, M, N), and it is clear that both with his glass and in the best of his quartz photographs Müller was getting more detail than did Stokes. The line called O by Esselbach, which designation Müller adopts, is, he considers, without doubt the one called by Stokes p, while the ones called by Esselbach P, Q, R, and S do not appear in Stokes' drawing but are found by Müller with his quartz spectrograph. One is a little disappointed to have no reproduction of these photographs, concerning which Müller says that they would have been reproduced in his publication, had it not been a matter of great difficulty to represent them exactly either on a copper-plate engraving or lithograph.

§ 26. 1859 and 1860 : Explanation of the Reversal of Spectral Lines, and the Firm Establishment of Spectrochemical Analysis (Kirchhoff ; Kirchhoff and Bunsen).—The first report given by Kirchhoff on the subject was communicated to the Academy of Sciences in Berlin in October, 1859, when he described the phenomenon of the reversal of lines. He says (the text has been freely translated by me throughout) : " Fraunhofer has remarked that in the spectrum of a flame there are two bright lines which coincide exactly with the two dark lines D of the spectrum of the sun. One gets the same bright lines, only brighter, in a flame into which one introduces common salt. I produced a sun spectrum and let the rays of the sun, before they fell on the slit, pass through a strong flame with common salt in it, and in place of the two dark D lines, two bright lines appeared. If, however, the sunlight is sufficiently bright the two dark lines appear much more distinctly, as if the flame with the salt therein had been absent."

Kirchhoff then describes how by using a lithium flame in the sun spectrum new dark lines could be seen, and continues :

" I deduce from these observations that coloured flames in whose spectra there are bright sharp lines weaken rays of the same colour as these lines when the same rays pass through those flames to such a degree that in place of the bright lines, dark ones are seen there, as soon as behind the flame a light-source of sufficient intensity is put, in whose spectrum those lines are not present. I conclude, therefore, that the dark lines of the sun spectrum, at least those which are not produced by the earth's atmosphere, indicate the presence of the same material in the sun's atmosphere as appeared in the same place in the spectrum of the flame.

"One can assume that the bright lines in the spectrum of the flame corresponding with the D lines of the solar spectrum originate from sodium. The presence of the dark lines D in the sun spectrum bring one to the conclusion, therefore, that sodium exists in the sun's atmosphere.

"Brewster found bright lines in the spectrum of the flame of saltpetre in the position occupied by the Fraunhofer lines A and B. These lines indicate the presence of potassium in the sun's atmosphere.

"I have not observed any dark line in the spectrum corresponding with the bright lithium line, and it would therefore appear probable that there is no lithium in the sun's atmosphere, or if any, only a relatively small amount."

Kirchhoff remarks also that a reversal of the lines only occurs when the absorbing flame is weak relative to the emitting source. With a Bunsen flame one cannot observe the dark D lines in the spectrum of a limelight; only with an alcoholic flame.

§ 26.1. A very similar observation had been made a little earlier by Foucault. Foucault's discovery is mentioned in the course of a paper published in *L'Institut* of February 7th, 1849, and a translation of Foucault's discovery was communicated by G. G. Stokes (1860) to the *Philosophical Magazine* together with a translation of the copy which Kirchhoff had sent to him of the report referred to *above*.

According to Foucault's communication he caused an image of the sun, formed by a converging lens, to fall on a voltaic arc formed between charcoal poles, so that he observed in his spectroscope electric and solar spectra superposed; he thus convinced himself that the double bright line of the arc coincides exactly with the double dark line of the solar spectrum. Stokes appends a characteristic note: "That remarkable phenomenon discovered by Foucault and rediscovered and extended by Kirchhoff, that a body might be at the same time a source of light giving out rays of a definite refrangibility and an absorbing medium extinguishing rays of the same refrangibility which traverse it, seems readily to admit of a dynamical illustration borrowed from sound. We know that a stretched string, which on being struck gives out a certain note (suppose it is a fundamental note), is capable of being thrown into the same state of vibration by aerial vibrations corresponding to the same note . . . the optical application of this illustration is too obvious to need comment."

§ 26. 2. The following year Kirchhoff published his observations and theory in a comprehensive form (Kirchhoff, 1860). He says: "The conclusion was long ago arrived at that at the same temperature the relation between emissive power and absorptive power is the same for all bodies. In this it had been assumed that the bodies send out rays of only one kind. This was established, in particular by Provostaye and Desains, by experiment in many cases, in which the similarity of the emitted rays could be assumed approximately in so far as the rays were dark." The following are among the more important of Kirchhoff's observations and deductions:

"The intensity of the rays of a given wavelength which are sent out by bodies at the same temperature can differ greatly. It is proportional to the absorptive powers of the body for rays of the wavelength in question. Metals, for example, glow much more intensely than glass at the same temperature, and glass more than a gas. A body which at the highest temperature remains entirely transparent will not glow." (*Translation.*)

Concerning the conditions necessary for producing the reversal of lines, Kirchhoff says that if one brings between a continuous light-source and the slit of the spectroscope a lithium flame, the brightness of the spectrum is altered only in the region of the lithium line. That line increases the brightness of the spectrum by its own light but reduces it through absorption. Assuming the absorption to be one-quarter, then according to Kirchhoff's law the lithium line will also be one-quarter as bright as the light of the same wavelength from a black body at the same temperature.

If the emitting body is a black one at the temperature of the lithium flame, the lithium flame will absorb a quarter of the light incident on it, but will itself send out as much, and will therefore remain without influence on the spectrum. If the continuous spectrum is, in the part in question, weaker than that of a black body of the same temperature as the flame, either because it emits less or because its temperature is lower than that of the flame, the flame will absorb less than it emits, and a bright line will be seen on a continuous background. If, however, the continuous spectrum is stronger than that of a black body of the temperature of the flame because its temperature is higher, the flame will absorb a quarter of that, which is more than it itself emits, and dark lines will be seen on a bright ground. Thus it is a sufficient condition for reversal that the absorbing flame should be colder than the emitting body.

"All spectra can be reversed. An exception can only come about with a flame in which a part of the light is produced by chemical process or with a flame that fluoresces. Experiment alone can determine whether such a flame exists." (*Translation.*) This last statement implies that Kirchhoff's law holds only where the emission is due to heat.

Kirchhoff continues: "The wavelengths at which maxima of emission and absorption power occur are in the highest degree independent of the temperature. Further, it is the metals which determine the maxima produced by salts in flames. From this it results that one can conclude with certainty that the presence of the D lines in the solar spectrum proves the presence of sodium vapour in the sun's atmosphere. They cannot originate in the earth's atmosphere, since:

1 In the earth's atmosphere there is not sufficient sodium vapour.
2. If they originated in the earth's atmosphere, then as the sun goes down they would get considerably stronger; this is not the case, although neighbouring lines (originating from the earth's atmosphere) do become more obvious.
3. If they originated in the earth's atmosphere, D lines would also be seen in all fixed stars, and both Fraunhofer and Brewster observed that not to be the case."

"A way is therefore found to make a determination of the chemical constitution of the sun's atmosphere, and the same promises a future for chemical determination of the fixed stars." (*Translation.*)

§ 26. 3. The assurance of Kirchhoff's statement that the presence of *metals* in a flame was proved conclusively by the presence of certain lines was justified by facts which at that time were in his knowledge but were published only later. There had been plenty of statements previously that one could, from the spectrum, carry out a chemical analysis, but no one had given a satisfactory proof of it by actual experiment with the spectroscope on known substances. Till then investigators had been satisfied to try one or at most two salts of an element in the flame without settling definitely whether, for example, the red line which was obtained by the use of lithium chloride was due to the lithium or the salt.

But Kirchhoff was justified in coming to the above conclusion, for he already had in his possession evidence from work then being carried on with the collaboration of Bunsen. The result of this work was first published three months later. In the first of their publications on this subject Kirchhoff and Bunsen (1860) were concerned with the three alkali metals then known : lithium, sodium, and potassium, and with the alkaline earth metals : calcium, strontium, and barium. Various salts of these elements were brought by them on a platinum wire into the flame. They had the advantage of being able to use what their predecessors had not had, the non-luminous flame of the Bunsen burner. The spectroscope (Fig 6) consisted of a prism of carbon bisulphide *F*,

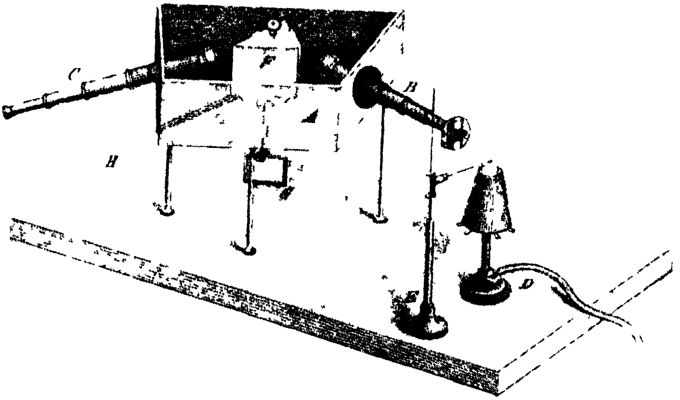

Fig 6.—Kirchhoff and Bunsen's Spectroscope (1860)

which could be turned by the help of the arm *H*. Below this handle and movable with it was a mirror *G*, on which a telescope, not seen in the figure, could read the reflection of a scale, so that readings of the rotation of the prism could be made corresponding to the wavelengths visible in the telescope *C*. It was observed that no matter what kind of flame was used (and a great variety were tried), the different flames and their great differences of temperature had no influence whatever on the position of the particular lines corresponding to the particular metals. Finally they also tried sparks between the electrodes of the metal, and found in the spectra so produced the same lines as in the flame, [illegible] accompanied by other lines, which they ascribed in part to impurities and in part to the nitrogen in the surrounding air.

The authors were able to announce that by the sensitiveness of the method they had already found a new member of the alkali group, namely cæsium. The following observation is also of interest :

" In the spectrum of a platinum wire made to glow in a flame, one can get the dark line D if one holds in front of it a glass on whose wall a little sodium amalgam has been brought and heats it to boiling-point. This experiment is important, for it shows that far below the temperature of glowing of sodium vapour, its absorbing effect comes into play."

Soon afterwards Kirchhoff and Bunsen were able not only to confirm the discovery of cæsium (Kirchhoff and Bunsen, 1861), but also the discovery by the spectroscope of a fifth alkali metal, rubidium. In this paper the authors described improved apparatus which they had constructed, in which a scale was visible in the field of view of the telescope at the same time as the spectrum, so that the position of the lines could be more conveniently read (Fig. 7).

Another important improvement consisted in the introduction of a comparison prism, that is a small prism which could be brought into one half of the slit to reflect light into the apparatus from a second light-source.

It will be seen that this instrument is indistinguishable in principle from many still supplied for chemical laboratories to-day.

One further remark by the authors was only fully appreciated in later years. They say : " Among the great number of the salts we have examined which are suitable for spectrum analysis in the flame, we have not met a single one which, in spite of the great variety of the elements combined with the metals, has not exhibited the lines of the metals. One can therefore assume that in all cases the lines of the spectrum of a substance are entirely independent of the elements with which they are associated." They say that one might from this be inclined to assume that the spectrum lines of a substance are always entirely independent of the elements with which the metals are combined, and that the spectrum of an element in chemical combination is always the same as when it is not in chemical combination and is in the uncombined condition. This assumption, however, would not be justified. The bright lines in the spectrum of a gas must, they repeat, correspond with the absorption lines which this gas produces in a continuous spectrum. They point out that the absorption lines of iodine vapour do not appear when one uses hydriodic acid, while on the other hand the absorption lines of nitrous oxide cannot be produced by a mechanical mixture of nitrogen and oxygen, and that it is possible that the influence of chemical combination on the absorption lines which in these examples is observable at a low temperature can also occur in the emission spectra at a glowing heat. If, however, combination in a gas alters its absorption lines, so must it also change its emission lines. Thus, although all the various salts of a metal which have been tried show the spectrum of the metal, it may be that this is so only because at the temperature of the flame these salts can no longer exist in combination, and that the vapour contains the metal which shows its lines. Thus, it is conceivable that a chemical compound can show lines other than those of the elements of which it consists.

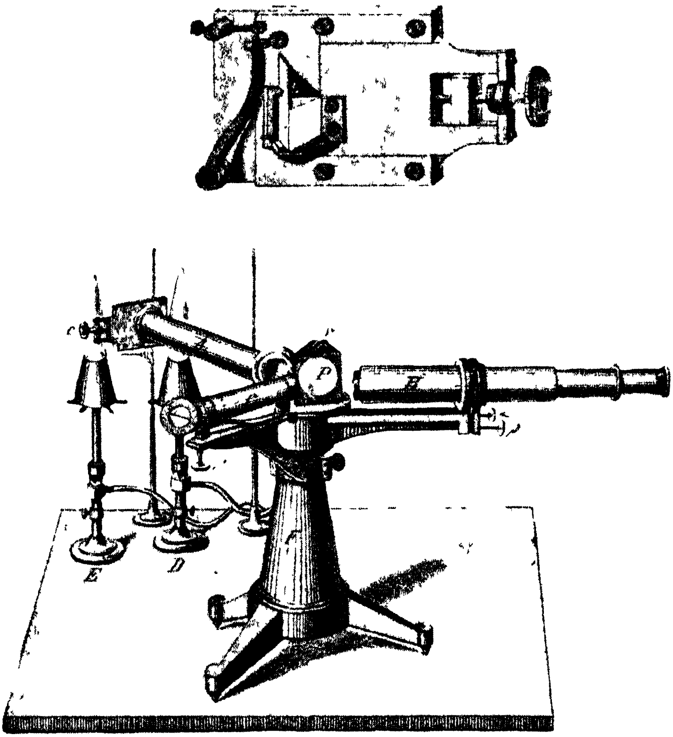

Fig. 7.—Kirchhoff and Bunsen's Improved Spectroscope (1861).

An example of the molecular spectra the authors saw to be possible is found in the background of the arc spectrum of a metal, which, as we now know, consists largely of the spectra of oxides of the metal.

§ 26. 4. Ångström (see under Thalén, 1869), in his measurements of wavelengths in the sun's spectrum, made so great an advance in the application of diffraction gratings for this purpose, that for the remainder of the century his measurements served for all spectral investigations.

Partly alone and partly in collaboration with Thalén, he compared 1000 lines of the sun's spectrum with lines of the elements occurring in the Earth. His measurements of the D lines, when corrected by a new value for the metre which he used in the measurement of his grating (Thalén, 1885), were 5895·13 and 5889·12 A., as compared with the most modern results, 5895·923 and 5889·949 A. (in air).

The gratings used by Ångström were made by Nobert of Barth.

§ 27. We see that in 1861 there was already available an efficient spectroscope, and a knowledge of how to produce the spectra of substances and of how to interpret them as evidence of the presence of metals; while discoveries such as those of rubidium and cæsium, thallium, and indium soon showed the power of the new tool.* But although spectrochemical analysis became one of the customary operations in the laboratory of Bunsen as a new aid in qualitative analysis, and although since that time there have always been a few workers who had constant recourse to the spectroscope in their daily work,† yet the original expectation that the new method would immediately find use as a general method of qualitative analysis became lost sight of after Bunsen's time to such an extent that the majority of chemical students scarcely ever use a spectroscope at all, even to-day. The position is now rapidly changing, largely as a result of the requirements of the metallurgical industries, in which during the past ten years spectrochemical analysis has become almost indispensable.

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* Rubidium and cæsium (Bunsen, 1860); thallium (Crookes, 1861); indium (Reich and Richter, 1864).

† Indeed, Lecoq de Boisbaudran (1874) wrote as the opening words of the text of his atlas of spectra: "Le spectroscope est maintenant l'auxiliaire indispensable de tous les chimistes"! More than one atlas had been published before this, but none approaching this one in scope or accuracy. The author maps out the spectra of about twenty-seven metallic salts, using a one-prism spectroscope. Both flame and spark spectra are given, and the results recorded in a series of twenty-eight beautifully reproduced plates and a calibration curve "représentant le rapport des longueurs d'ondes aux divisions de mon micromètre."

The "micromètre" was a photographic divided scale, the image of which was reflected on to the second face of the prism, and was thus seen in juxtaposition to the spectrum (Kirchhoff and Bunsen's arrangement is shown in Fig. 7).

There were numerous reasons for this neglect of the method. Firstly one may mention the extraordinary sensitiveness of the method in certain cases. Unless one takes the utmost care it is impossible to get rid of the two yellow lines of sodium whatever substance one is examining, and this is only an extreme case of what often happens in spectroscopy. Thus, in many cases spectrum lines would show in which the chemist might have no interest.

Again, in the use of a particular spectroscopic routine it was only certain of the elements that showed this extraordinary sensitiveness, others scarcely revealing their presence. For instance, in the Bunsen flame only the alkali metals show with intensity. The alkali-earth metals, as well as indium and thallium, show feebly, while other metals do not show at all. It is true that it was known quite early that metals in general in the spark revealed their presence by their characteristic spectra, but convenient means of providing electric current were not generally available for many years after 1861.

When the spark and arc spectra became available by the extension of electrical facilities, there was a third deterrent to the use of the spectroscope, for many of the elements gave spectra very rich in lines, and little characteristic to a casual glance. The unravelling of such a maze of lines might well seem more difficult and tedious than the full routine of chemical analysis. Again, there was no known quantitative relation between the appearance of the lines of a metal and the percentage present in the substance examined.

Photography has now become so familiar to everyone that its employment as a laboratory routine is customary ; but fifty years ago this was not the case, and there is no suitable means, other than photography, of observing or recording the ultra-violet spectrum which is so valuable in spectrochemical analysis.

In 1893 Rowland published his first *New Tables of Standard Wavelengths*, which gave, for the first time, the wavelengths of reference lines with the accuracy needed for identification of substances which have complex spectra ; but it was not till a good deal later that tables of the wavelengths of the elements became readily available.

All the more customary flame examinations can be performed with the very simplest of instruments, such as the Bunsen and Kirchhoff spectroscope. Such an instrument is excellent for the detection of the alkali metals by their flame spectra, but it is of little use for general metallurgical work ; and it was not until about 1909 that quartz spectrographs of a convenient kind could be bought.

§ 28. Thus, although spectroscopy developed, it was mainly under the auspices of the physicist and the astronomer. For these it rapidly became an instrument of supreme importance, but in the academic laboratories it was chiefly used, if at all, as a means of teaching optics, and instruments were deliberately made with as many adjustments as possible in order that the students might learn the principles of the instrument rather than its use as an implement of research. These are doubtless some of the obstacles which delayed the general adoption of spectrochemical analysis. One astronomer, J. Norman Lockyer, did indeed turn aside to give a glance at the possibility which the spectroscope offered to the analyst.

§ 28.1. 1873 and 1874 : Observation of the "Long" and "Short" Lines, and the First Quantitative Spectrochemical Analysis (Lockyer; Lockyer and Roberts).—In three papers Lockyer (1873*a*, 1873*b*, 1874) made observations which have proved of lasting interest.

Lockyer's investigation was directed to a study of the sun, and his studies of terrestrial sources were only supplementary to his main interest, which was astronomical. He found that if he formed an image of a spark on the slit of a spectroscope, so that each spectrum line along its length represented the radiation from different points between the electrodes, some of the lines were short, in the sense that they were located only in the neighbourhood of the electrodes, while others extended throughout the entire length between the electrodes. He found that the flame spectrum of the same metal yields only those lines which in a spark are long ones. He found, too, that if he produced the spark and reduced the atmospheric pressure, it was the long lines which remained visible longest.

In the third of the papers cited Lockyer says : "While the qualitative spectrum analysis depends upon the position of the lines, the quantitative analysis depends not upon their position, but upon their length, brightness, thickness and number as compared with the number visible in the spectrum of a pure vapour" ; and later, in a section headed *The Experiments made on a Possible*

Quantitative Spectrum Analysis, he points out that: "Since, beginning with an alloy giving only the longest lines in the spectrum, by increasing the constituents other lines can be produced in the order of their length, the measurement of their length might give a measure of the quantity present".

§ 28. 2. It will be seen that in the above passages Lockyer adumbrates several possible quantitative methods. Lengths of lines have since been used by Occhialini (§ 124); the measuring of the brightness of the lines is, of course, the foundation of most of the methods in use to-day; while the thickness of the lines has been used by Eisenlohr and Alexy (§ 141. 1), and the number visible was the foundation of Hartley's method (§ 29).

Lockyer attributed the variations in the lengths of the lines to differences in the volume occupied by the vapours of the metal. It is certain that this is not the only reason, but no doubt it participates in the phenomenon (§ 38).

Lockyer and Roberts (1874), using the same arrangement, namely an image of a spark on the slit, attempted to base a quantitative method on one of the three following phenomena:

(1) Changes in the lengths of lines of one constituen

(2) Changes in the position of the point at which lines belonging to different metals in the alloy show equal brightness or thickness.

(3) Changes in the relative lengths of a pair of lines belonging severally to the constituents of the alloy.

The last-named suggestion implies an appreciation of the principle of the "internal standard" (§ 117).

The authors' words may be quoted with regard to one example: "A number of alloys of zinc and cadmium were synthetically prepared, and from these a series of five, the proportion of cadmium in which increased by 1 per cent. from 50 per cent. to 54 per cent., were carefully selected for the experiments . . Observations by means of the spectroscope at once enabled us to arrange these alloys in the correct order." That they should have been able to do this is surprising, and it would be worth while repeating their experiments with other alloys. Their care to select for their experiments an alloy which was homogeneous may be noted in connection with the interest which has in the last few years attached to the question of heterogeneity as a cause of discrepancies between chemical and spectrochemical analyses.

§ 29. The Revival of Spectrochemical Analysis (Twyman and Smith, 1931*).—The resuscitation of spectrochemical analysis is to be referred primarily to two workers—W. N. Hartley (with his assistants) and A. de Gramont.

Hartley, working at the University of Dublin, first noted that it is not always the strongest lines of an element which are the most persistent when that element is present in a substance in small and decreasing amounts. Already in 1882 he had investigated the proportions of certain metals which would be evidenced in compounds by the presence of their lines in the spectrum, and had as a result estimated the amount of beryllium contained in certain cerium compounds. He preferred to work with solutions, and used the spark condensed by a Leyden jar. Hartley's work was continued, also at Dublin, by Pollok and Leonard, and this group of workers studied a large number of metals in solution.

Pollok and Leonard distinguished the lines of each particular metal by Greek letters, which showed the persistence of the spectrum line as the quantity of metal present was reduced according to the following system :

TABLE II.—POLLOK'S NOMENCLATURE FOR THE SENSITIVE SPECTRUM LINES OF METALS IN SOLUTION AS PHOTOGRAPHED ON A MEDIUM QUARTZ SPECTROGRAPH.

Line.	Seen with	But not seen with :
τ	Metal.	Strong solutions.
σ	Strong solutions.	1 per cent. solutions.
φ	1 per cent. solutions.	0·1 per cent. solutions.
χ	0·1 per cent. solutions.	0·01 per cent. solutions.
ψ	0·01 per cent. solutions.	0·001 per cent. solutions.
ω	0·001 per cent. solutions.	

In this way Hartley and his coworkers laid the basis of an approximate quantitative spectrochemical analysis, and although it is only in rare cases that this method can compare with the balance, it provides a means of readily distinguishing between a considerable percentage of a material and mere traces only, of which Hartley made some interesting use. Ramage (1929 ; Ramage,

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* This reference contains full bibliographies of the publications on the subject by Hartley, Pollok and Leonard, and de Gramont.

Sheldon and Sheldon, 1933), who worked under Hartley, on his retirement devoted his attention to analysis by flame spectra, and a method he adopted, as improved by Steward (§ 139), seems likely to prove of permanent use. More important still, owing to the work of the Dublin school, it was thereafter unnecessary in hunting for a small quantity of an element in a sample to look for any but the few lines known to be persistent.

The work of A. de Gramont (§ 112), at the Sorbonne in Paris, was of a similar character, and he also used the condensed spark, but he worked chiefly with solids.

§ 30. All these observers agree on the importance of noting those lines which are still shown when an element is present in a substance in very feeble quantity. These were called by Hartley, Pollok and Leonard *persistent lines.* De Gramont called them *raies sensibles,* while those remaining last of all when the amount is decreased he called *raies ultimes* (§ 39). These rays present the following characteristics :

(1) They are not necessarily the strongest lines in the spark spectrum of the element.

(2) They are present in the spark, but belong to the arc spectrum of the element, where they are generally of great intensity.

(3) They are generally present also in the spectra of very hot flames (oxy-hydrogen or oxy-acetylene).

A number of de Gramont's lines are given in Table III (Twyman and Smith, 1931).

A. de Gramont finds these conclusions to hold for alloys, minerals, and fused salts, and states that his observations are in general agreement with those of Pollok and Leonard in the case of solutions, which greatly increases the value of the tables of all these observers. But Hartley, Pollok and Leonard give lines which de Gramont omits in his summary, and *vice versa* ; thus it is wise to refer to the tables of both sets of workers. De Gramont, for instance, in his summary omits among others the useful nickel lines 3050·9 and 3054·4.

On the subject of *raies ultimes* the reader should also refer to § 113.

The order of sensibility is that found by photography, either with a medium quartz or with a " Uviol " crown-glass spectrograph, and it is in the ultra-violet that the " raies ultimes " almost always lie. But where " raies sensibles " are recorded in the visible spectrum they are often of high sensibility for the eye.

TABLE III.—" RAIES DE GRANDE SENSIBILITÉ ET RAIES ULTIMES DES ÉLÉMENTS."

(All wavelengths are in international angstroms, A.
Figures in heavy type indicate *raies ultimes*.)

Element.		À l'observation oculaire :	Par la photographie :	
			Spectrographe *crown uviol.*	Spectrographe *quartz.*
Mo	Molybdene .	5570,5 ; 5533,2 ; 5506,5	**3903,0**$_u$ (1) ; **3864,1**$_u$; **3798,3**$_u$ (1) ; 3635,2	
Nd	Néodyme . [3]	. . . . .	4303,6 ; 4177,3 ; 3951,2	
Ne	Néon . [1]			
Ni	Nickel .	5476,9 ; 5081,1 ; 4714,4	3619,4 ; 3524,5 ; 3515,1 ; **3414,8**$_u$; 3380 6	2437,9 ; **2416,2**$_u$; **2316,1**$_u$; **2303,0**$_u$
Au	Or . .	6278,2 ; 5837,4 ; 4792,6	. . . . . .	2802,2 ; **2676,0**$_u$; **2428,0**$_u$
Os	Osmium . [1]			
O	Oxygène . [2]			
Pd	Palladium . [4]	5547,0 ; 5295,6 ; 5163,8	**3634,7**$_u$; **3609,6**$_u$; 3421,2 ; **3404,6**$_u$	
P	Phosphore .	. . . .	. . . . . .	2555,0 ; **2553,3**$_u$; **2535,6**$_u$; 2534,0
Pt	Platine . [3]	5475,8 ; 5390,8 ; 5301,0 ; 5227,6	**3966,4**$_u$; 3923,0 ; 3268,4 .	3064,7 ; 2929,8 ; 2659,4
Pb	Plomb .	5608,9 ; 5005,5 . .	**4057,8**$_{u1}$; **3683,5**$_{u2}$; 3639,6	2614,2 ; 2203,6 ; 2175,8
K	Potassium .	7699,0 ; 7669,4 ; 5832,0 ; 5801,8 ; 5782,4	**4047,2**$_{u1}$; **4044,2**$_u$; 3447,4 ; 3446,4	
Pr	Praséodyme [1]			
Ra	Radium . [1]	. . . . .	(4825,9 ; 4682,2 ; 3814,5) (2)	
Rh	Rhodium . [4]	. . . . .	3799,3 ; 3692,4 ; 3658,0 ; **3434,9**$_u$	
Rb	Rubidium .	7947,6 ; 7800,3 . .	**4215,6**$_{u2}$; **4201,8**$_{u1}$	
Ru	Ruthenium [4]	. . . . .	**3499,0**$_u$; 3436,7	
Sa	Samarium . [1]			
Sc	Scandium . [4]	. . . . .	4246,9 ; 3651,9 ; **3630,8**$_u$; **3613,8**$_{u1}$	
Se	Sélénium . [2]			
Si	Silicium .	6370,9 ; 6346,8 . .	3905,5	**2881,6**$_u$; 2528,5 ; **2516,1**$_u$; 2506,9

[1] Non études par l'auteur.
[2] Ne donnant ni raies ultimes ni raies de grande sensibilité.
[3] En cours d'etude ; résultats provisoires.
[4] Etudies seulement au crown uviol ; résultats provisoires.

(1) Masquées par des raies du fer.
(2) Runge et Precht.

The instruments with which Hartley and de Gramont worked in the first instance, although quartz spectrographs, were not of the modern convenient kind, and entailed manipulations of a nature not generally familiar.

§ 31. Shortly before 1904 I became strongly conscious of the need for more convenient and labour-saving spectroscopes, and in that year utilized a form of prism, invented by Abbe and already made known by Broca, to design the now well-known constant-deviation wavelength spectrometer. This is a visual instrument in which there is no divided circle, the telescope and collimator being fixed, and the prism being rotated by a micrometer screw, on the large head of which wavelengths of the lines under observation are engraved. This type of instrument is now made by all the makers mentioned in § 56.

§ 32. The work done by de Gramont, and by Hartley, however, made it obvious that for general use a convenient photographic instrument was needed, and in 1909 I designed the fixed-adjustment medium quartz spectrograph, in which, by a mixture of simple calculation, experiment, and, perhaps, good luck, I succeeded in getting the whole photographic spectrum in fairly good focus on a flat photographic plate. It was one of these instruments which was used by Pollok, Leonard, and Ramage, and indeed by Hartley in his later work; another, with prism and lenses of "Uviol" glass, was used by de Gramont.

In 1912, in order to deal more readily with the very complex spectra of steels, I designed a large quartz spectrograph, giving three times the dispersion of the medium one. These quartz spectrographs have been greatly improved in construction and definition in the ensuing years, but in general design and in optical dimensions all the makers mentioned in § 56 follow these two instruments very closely.

Precisely when History ends may be difficult to define on general principles, but to me the "history" of spectrochemical analysis ends with the investigations of Hartley and of A. de Gramont; it was then that the "modern times" of the subject commenced. Incidentally, the good fortune whereby spectrographs of my design were used by these investigators was probably the reason why I have been involved, implicated, entangled—whichever may be the right word—in the subject to-day.

CHAPTER II.

THE ELEMENTS OF ATOMIC SPECTRUM THEORY.

Types of Line Spectra and their Structure.

§ 33. Introduction.—Modern study of spectra has shown that the lines due to an element, which seem to be scattered haphazard, are actually distributed according to surprisingly simple laws. Take, for example, the spectrum of lithium, shown in Fig. 8. The lines shown in the top strip appear scattered at random, but analysis shows that they all belong to one of four series, and when these are separated the lines of each series appear spaced in a regular way. Further study shows that not only are the wavelengths of the lines in each series simply related, but the different series are also related one to another.

While this theoretical study of atomic spectra has not been of any considerable use in building up the present effective technique of spectrochemical analysis, for almost all important advances have been empirical, the nomenclature of theory is now sometimes found in papers dealing with analysis, while, as we shall see later, the theoretical knowledge about line spectra has practical applications in spectrochemical analysis, which may become of increasing importance.

§ 34. Series in Hydrogen.—A general relationship between the lines of a series was first discovered by Balmer. When an electrical discharge from the old-fashioned induction coil is passed through a vacuum tube containing hydrogen at low pressure four lines appear in the visible spectrum. Balmer's discovery consisted in showing that the wavelength λ of a line is given by the formula

$$\frac{1}{\lambda} = \nu = R\left(\frac{1}{2^2} - \frac{1}{n^2}\right),$$

where ν, the reciprocal of the wavelength in cm., is known as the wave-number, and R is a constant ; n assumes the values 3, 4, 5, and 6 in successive lines.

The four visible lines of the Balmer series show features which are characteristic of series in all elements :

(*a*) the lines grow less intense as one passes from the longer to the shorter wavelengths ;

(*b*) the spaces separating successive lines decrease towards the shorter wavelengths in such a way that if many lines appear in a series, the latter tends to a well-defined limit.

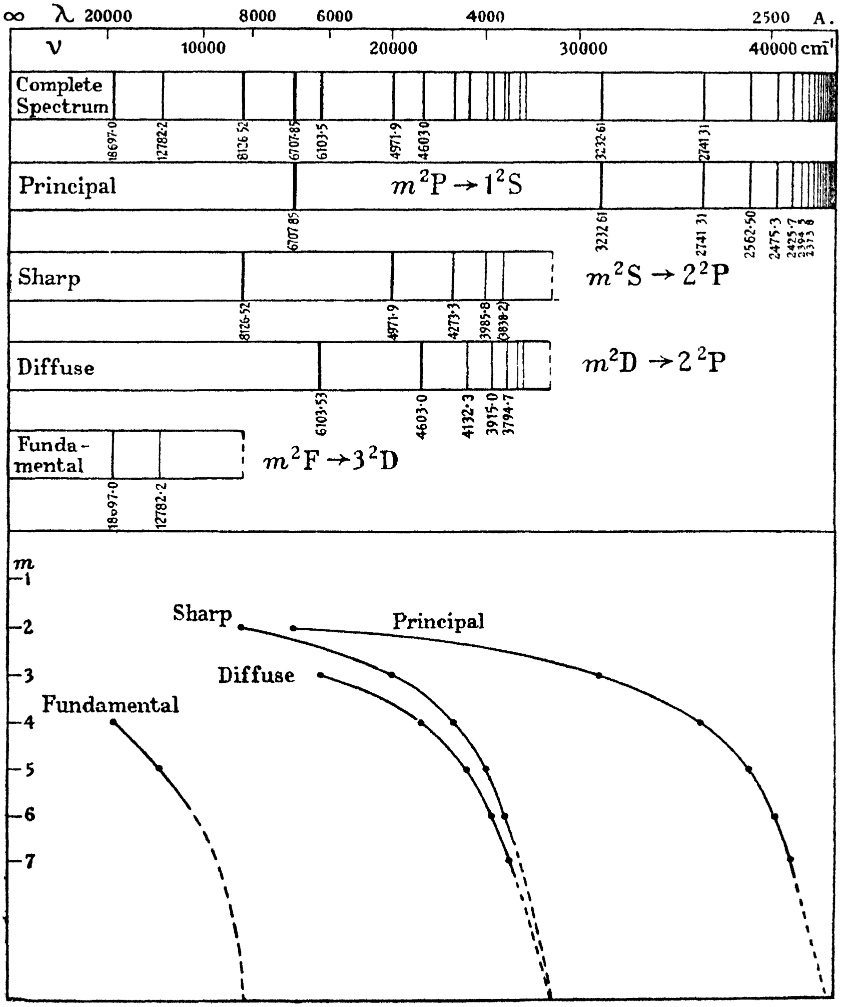

Fig. 8.—Series in Lithium (Candler, 1937*a*). The scale is a uniform scale of frequency ; the lower part illustrates Rydberg's series formula.

Later workers measured many lines in the ultra-violet, and found that these also fit the formula with remarkable accuracy, when n is given higher integral values. If R is taken as 109,678·72

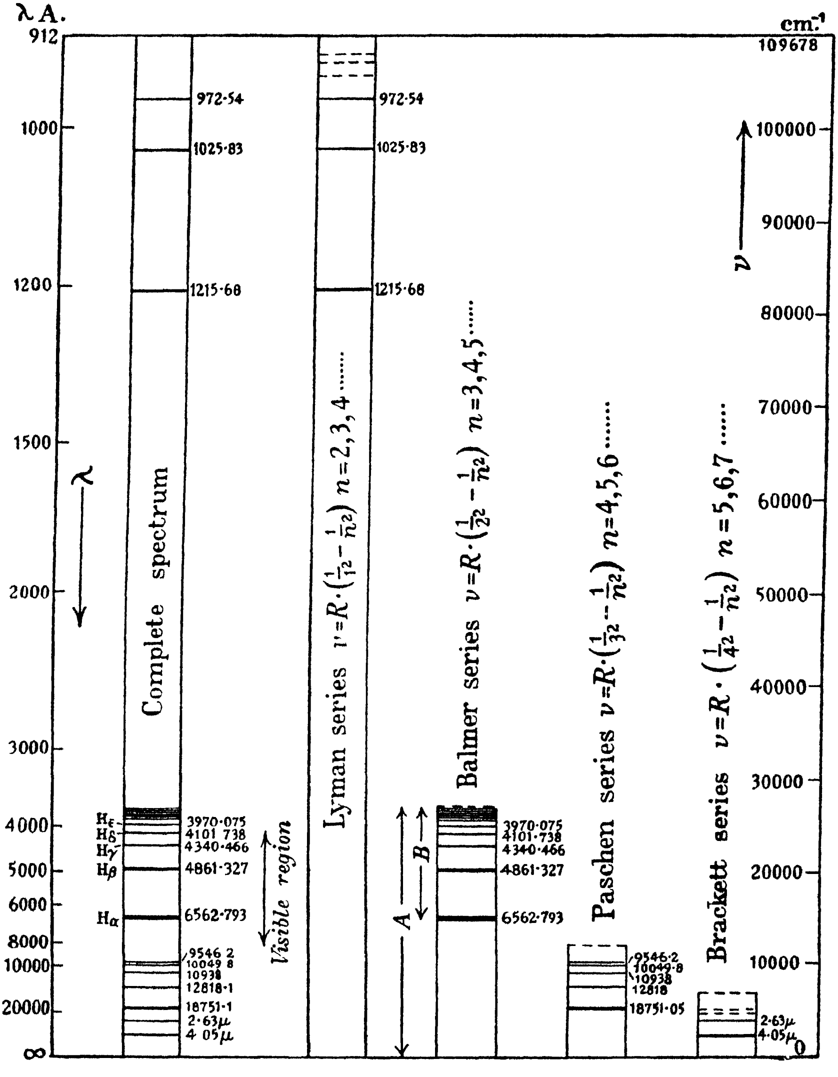

Fig. 9.—Spectrum of Hydrogen. After Grotrian, *Graphische Darstellung der Spektren.*

cm.$^{-1}$, the biggest discrepancy between the calculated and observed wavelengths for the first six lines of the series is only three parts in a million.

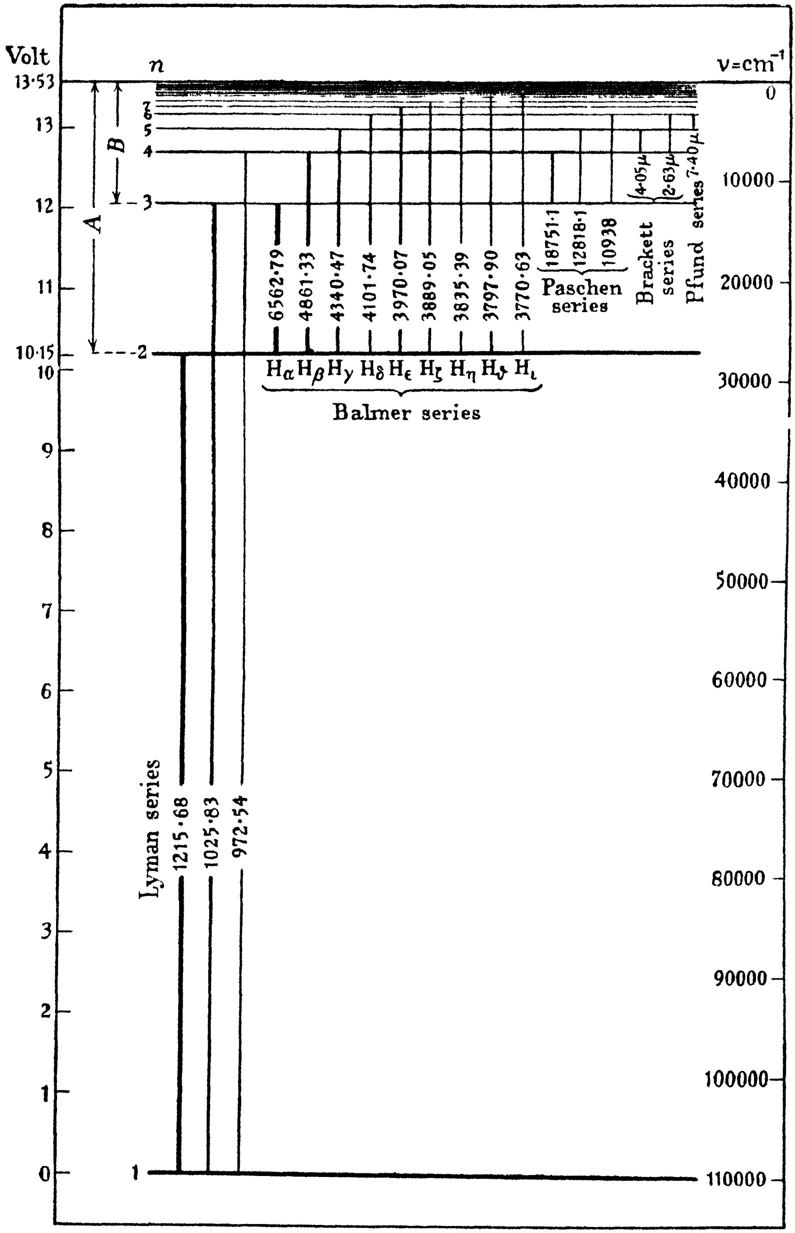

Fig. 10.—Level Diagram of Hydrogen. Each vertical shows an electron jump; the numbers give the wavelength in angstroms, the thickness gives a rough indication of the intensity.

Later Lyman found another series of hydrogen lines in the far ultra-violet, while Paschen, Brackett, and Pfund observed new series in the infra-red (Fig. 9). Generalized in the form

$$\nu = R\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right),$$

the formula showed itself capable of accounting for all these new series ; indeed it was used to predict some of them. n_1 is fixed for any given series, and has the values 1, 3, 4, 5 for the Lyman, Paschen, Brackett, and Pfund series respectively, while n_2 takes on a series of integral values, the lowest of which is $(n_1 + 1)$. The limit of any series is obtained by making n_2 infinite, so that the limit of the Balmer series is simply $R/4$, or 27,419·7 cm.$^{-1}$.

These facts are simply illustrated by a diagram due to Grotrian (Fig. 10). Down a vertical line lengths R, $R/4$, ... R/n^2 are measured off, and horizontal lines are drawn through the points obtained to represent the values of these terms. Later it will be shown that these terms represent energy states of the atom. Any transition between two terms may be represented by a vertical arrow, whose length will be a measure of the frequency of the line emitted. The H_a line, whose wave-number is given by the equation

$$\nu = R\left\{\frac{1}{2^2} - \frac{1}{3^2}\right\},$$

may be used to illustrate this ; in both Figs. 9 and 10 it appears as the difference of two lengths marked A and B, which are in fact the quantities $R/4$ and $R/9$; but whereas in Fig. 9 they are measured from the limit of the Balmer series, in Fig. 10 they are measured down from a line which is the limit of the term sequence, being the value of R/n^2 when $n \rightarrow \infty$.

Fig. 10 may be refined to give an even clearer picture of a series, by so spacing the arrows horizontally that if the spectrum lines to which they correspond are shown at the bottom, these are correctly spaced along a frequency scale with the highest frequency on the right. This has been done for the Balmer series in Fig. 11.

§ 35. Atomic Energy Levels.—In the decade which succeeded Balmer's discovery Rydberg discovered a formula which can be made to fit series in every element ; what the formula gains in generality, however, it loses in simplicity, for it contains two constants, which must be varied from series to series.

Rydberg's ultimate purpose was to gain a knowledge of the structure of atoms and molecules, but although a great deal was done by him and other workers in discovering numerical relationships between the frequencies of spectrum lines, and in showing the connection between different series in a single spectrum, little progress was made towards the fulfilment of that purpose until 1913. In that year Bohr put forward two principles of fundamental importance.

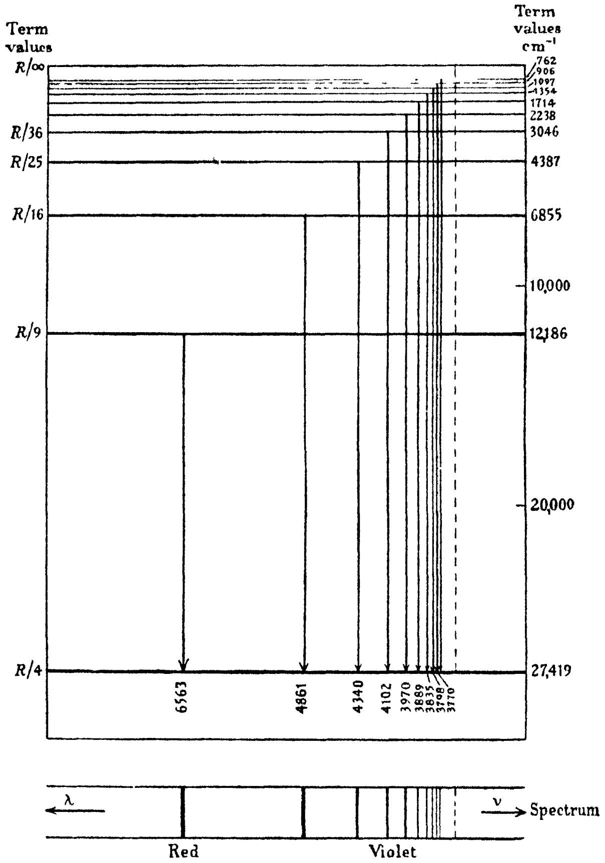

Fig. 11.—Level Diagram of the Balmer Series. The spectrum shows the lines on a uniform scale of frequency.

Rutherford had shown that experiments on the scattering of α-particles could best be explained by assuming each atom to consist of a number of negatively charged electrons revolving round a positively charged nucleus. The total negative charge of the electrons is equal to the positive charge on the nucleus, and nearly the whole mass of the atom is concentrated in the nucleus.

Now Planck had already shown that the distribution of energy in the radiation from a black body could not be explained by the classical theory which assumed that the radiation is continuous; instead he assumed that energy is emitted in discrete pulses or "quanta," and that if a particular pulse has a frequency ν', then its energy is $h\nu'$, where h is a universal constant known as Planck's radiation constant.

Bohr combined these two theories, and found that from two postulates he was able to derive an expression for the frequencies which should be emitted by a hydrogen atom; this expression is identical in form with the generalized Balmer formula, and gives an equation for R in terms of other physical constants (Candler, 1937*a*, p. 12); the numerical agreement between this expression and the experimental value of R is important evidence in favour of Bohr's theory.

The importance of the advance from Balmer's numerical relationship between the frequencies of the lines to an explanation of these frequencies in terms of changes occurring in the atom can hardly be exaggerated. The advance depends on two postulates. The first of these states that an electron can revolve round the nucleus only in certain orbits, such that 2π times the angular momentum of the electron is an integral multiple of Planck's constant h. Bohr called these orbits "stationary states," because only in these orbits can the electron remain for an appreciable time.

The second postulate adds that when an electron leaves one stationary state, it immediately passes to another, and that if these states have energies E' and E'', then on the electron passing from the state of greater energy E' to that of lesser energy E'' a quantum of monochromatic light of frequency ν' will be emitted, ν' being determined by the relation

$$h\nu' = E' - E''.$$

Absorption of light is the converse process; when radiation from a hot body passes through a gas or vapour, those wavelengths are absorbed which satisfy the equation, the atoms of the gas being raised from energy level E'' to level E'. The conception of stationary states and the quantum relation, which determines the frequency of the line produced when an atom passes from one state to another, are the solid rocks on which all later theories of the atom are based.

§ 36. Series in Lithium.—In the elucidation of simple spectra early workers depended almost entirely on the discovery of series of lines. The series have the same general appearance as the series of hydrogen ; the lines decrease in intensity and lie nearer and nearer together as the eye moves from the red to the violet. But these rules alone are seldom sufficient to identify the lines of a series, for in all spectra, except that of hydrogen, different series overlap one another. This is illustrated in Fig. 8, which shows the spectrum of lithium.

Sometimes the appearance of the lines helped early workers, and so the terms " sharp " and " diffuse " were used to designate particular series in the alkalis. Again, in lithium, which we may select as a type for this description, the lines of a third series are particularly intense and are easily absorbed by cold lithium vapour, so that it is known as the " principal " series. Often, too, lines of this series appear " self-reversed " ; that is to say, the normal line has a narrow dark line down the centre of it, an appearance which arises when the centre of the broad line emitted by the hot core of the discharge is re-absorbed by the cooler layers outside ; the line emitted will naturally be broader than that absorbed, because the Doppler effect of a moving source will broaden a line the more the greater the velocity of the source, and therefore the higher the temperature.

In the general equation for the series of hydrogen

$$\nu = R\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right),$$

the wave-number of the head of the series, which we may write T_l, is found by making n_2 infinite. Thus the equation for a particular series reduces to

$$\nu = T_l - \frac{R}{n_2^2}.$$

Rydberg showed that this may be generalized for the series of other elements in the form

$$\nu = T_l - \frac{R}{(m + a)^2},$$

where a is a constant characteristic of the series, and m assumes a series of integral values just as n did. m is commonly called the serial number. Rydberg's constant R has the same value in all spectra, if small deviations in a few light atoms are for the present ignored.

Unfortunately, though nearly all series obey Rydberg's law approximately, very few fit with the high accuracy of spectroscopic work, so that predictions which should be precise are only approximate. Attempts to improve the formula by the addition of further terms have no theoretical significance, and the modern spectroscopist contents himself with finding those values of T_l and a which render the deviations between the equation and the observed wavelengths as small as possible.

Rydberg's equation is of the same general form as the Bohr quantum theory equation

$$\nu = \frac{\nu'}{c} = \frac{E'}{hc} - \frac{E''}{hc},$$

so that each term of Rydberg's equation gives the energy of a particular state of the atom. All known energy levels are tabulated in Bacher and Goudsmit's *Atomic Energy States.*

When the values of the series limits are examined they are often found to be identical with the terms of other series. Thus the limit of the sharp series of lithium has the same energy as the lowest term of the principal series ; the wave-numbers of all lines of the sharp series are given by

$$\nu = \frac{R}{1{\cdot}96^2} - \frac{R}{(m + 0{\cdot}60)^2}, \qquad (m = 2, 3, 4, \ldots)$$

while the first line of the principal series is

$$\nu = \frac{R}{1{\cdot}59^2} - \frac{R}{1{\cdot}96^2}.$$

This line is the well-known red line of lithium, with a wavelength of 6708 A. and a wave-number of 14,904 cm.$^{-1}$; and, in fact, Bacher and Goudsmit give the energies of the $2P$ and $1S$ terms, from which it arises, as 28,582 and 43,486 cm.$^{-1}$ with a difference of 14,904. Here the terms are rather confusingly measured down from the energy required to ionize the atom, so that the higher $2P$ term has the smaller term value ; this is unfortunate, but in Bacher and Goudsmit's tables the lowest term is always placed first.

In the Rydberg formula a term can be specified by the values of the serial number m and the quantum defect a, m being always integral and a the same for all lines of a series. Thus the quantum defect may be conveniently written p for terms of the principal series, s for terms of the sharp series, and d for terms of the diffuse series. Thus the energy of the lowest term of the sharp series is $\frac{R}{(1+s)^2}$, where $s = 0{\cdot}60$; but this is clumsy and is commonly abbreviated to $1s$ or $1S$, where the number is the value of m, and S shows that the term belongs to the sharp series.

In this notation the lines of the sharp series of lithium quoted *above* are $mS \rightarrow 2P$, where the term with the greater energy is written first, and the arrow shows the direction of the change. Similarly, the first line of the principal series is written $2P \rightarrow 1S$; and the only reason why the transition from $1S$ to $2P$ is not a member of the sharp series is that in the alkalis the $1S$ state has less energy than the $2P$ state, so that the transition from $1S$ to $2P$ can appear only in absorption, when it is written $2P \leftarrow 1S$.

These facts are conveniently illustrated by an energy level diagram (Fig. 12). The levels might be shown by horizontal lines stretching right across the page, but the diagram becomes clearer if the levels belonging to different sequences are arranged on different verticals. The broken diagonals represent the transitions which have been observed, and in the break the wavelength of the resulting line is inserted. The thickness of the diagonal is roughly proportional to the intensity of the line.

The abbreviated equations are important, because in all spectra other than hydrogen transitions between different energy levels are restricted by "selection rules," and these depend on the sequence to which a term belongs. Thus if the S, P, D, and F term sequences are arranged in that order, each sequence may combine only with its neighbours; P may combine with S and D, but not with F; S may combine with P, but not with D or F. This rule derives from the observed fact that the four series commonly observed in the alkalis are:

the principal . .	$mP \rightarrow 1S$,	$m = 2, 3 \ldots$
the sharp . . .	$mS \rightarrow 2P$,	$m = 2, 3 \ldots$
the diffuse . . .	$mD \rightarrow 2P$,	$m = 3, 4 \ldots$
the fundamental . .	$mF \rightarrow 3D$,	$m = 4, 5 \ldots$

The lowest terms of the sequences are written $1S$, $2P$, $3D$, and $4F$, because in many simple spectra this notation gives the $4S$, $4P$, $4D$, and $4F$ terms roughly the same energy.

Theory generalizes this rule by introducing a quantum number L, defining the angular momentum of the electron as it revolves round the nucleus; in the sequences S, P, D, F, ... the quantum number *L* assumes the values 0, 1, 2, 3, ... Then the selection rule states that a transition is possible only when $\Delta L = \pm 1$

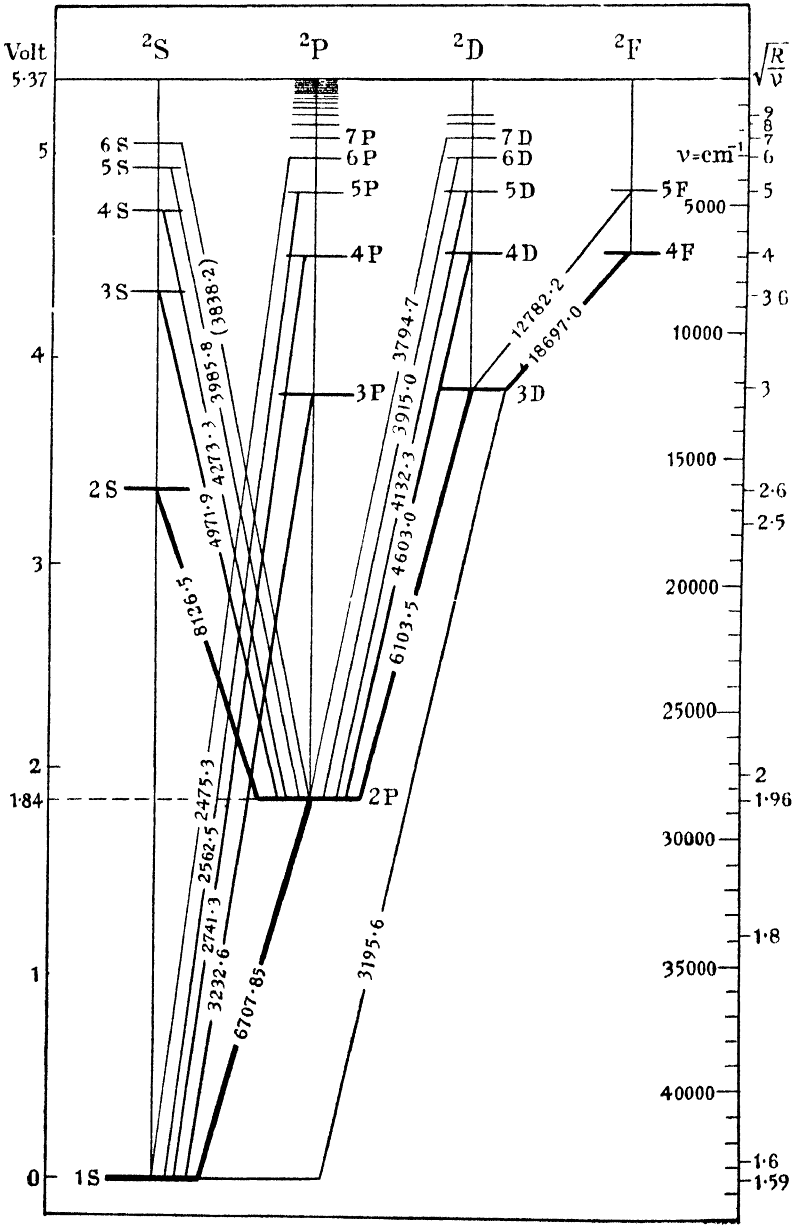

Fig. 12.—Level Diagram of Lithium, showing the Transition in which each Line arises.

(Candler, 1937*a*, p. 26). In complex spectra this selection rule appears as a particular example of a more general rule, which states that an "even" term can combine only with an "odd" term; "even" cannot combine with "even," nor "odd" with "odd" (Candler, 1937*b*, p. 4). To discuss what makes a term even or odd would take us too far afield; suffice it here to say that odd terms are commonly indicated by a degree sign, P° and F°. In Bacher and Goudsmit's tables all odd terms are printed in italics.

The higher the term in which a line arises the harder is that line to excite; in fact, Newman has excited the spectra of the alkalis with electrons which have fallen through a measured voltage, and has shown that the number of lines appearing in the spectrum increases as the voltage increases. For the same reason the red lines of a series, which arise in low levels, are more intense than the violet lines, which arise in high levels. In general the relative intensities of different lines in the spectrum depend on the method of excitation, but the relative intensities of the several components of a multiplet are the same however the multiplet is excited.

§ 37. Ionization Potentials.—When atoms are excited by electrons which have fallen through a controlled potential, and the potential is slowly raised, one finds that there is a certain voltage at which a single line is emitted, and a higher voltage at which electrons are emitted. The first is called the *resonance potential*, and the line emitted results from the return of an electron from the lowest level from which a return to the ground level is permitted; the second is the *ionization potential*, an electron being thrown right out of the atom, and is sufficient to excite all the lines of the arc spectrum.

Ionization potentials are important as giving a rough measure of the ease with which a spectrum can be excited. In the alkalis, for instance, the ionization and resonance potentials decrease from sodium to cæsium, and experiment shows that a Bunsen flame at 1550° C. emits two lines from lithium and sodium, three from potassium, four from rubidium, and six from cæsium. Further, in such flames, where the energy of the colliding atoms is low, many more atoms attain the resonance potential than the ionization potential, so that the first member of a series is much brighter than the higher members; the relative prominence of this line becomes less as the temperature is raised.

The ionization potential can be measured directly by allowing electrons to fall through a known voltage, and seeing whether any positive ions are produced (Candler, 1937*a*, p. 72); or it can be calculated from the series laws. Thus suppose that two lines of the principal series of sodium are known to have wavelengths of 5890 and 3302 A., then the Rydberg equation states that

$$\frac{10^8}{5890} = T - \frac{R}{(1+a)^2};$$

$$\frac{10^8}{3302} = T - \frac{R}{(2+a)^2}.$$

From these two equations T and a can be calculated, since R is known to have the value 109,737 cm.$^{-1}$; or more conveniently they may be read off from Rydberg's term table (Candler, 1937*a*, Appendix III). For the lines quoted T has a value of 41,449 cm.$^{-1}$. so that the ^2S level in which the lines end lies 41,449 cm.$^{-1}$ below the limit of the series. Now the ^2S level is the lowest or ground state of the sodium atom, while the limit of a series marks the point at which an electron is just removed from the atom, so that the work required to ionize the atom is 41,449 cm.$^{-1}$.

To convert energies in cm.$^{-1}$ into electron-volts is simple enough, if the charge on an electron and Planck's constant are known. The fundamental equation states that an electron carrying a charge e will liberate a quantum of frequency ν', it it has fallen through a potential difference E given by the equation

$$h\nu' = Ee.$$

Changing to wave-numbers or wavelengths, this becomes

$$E = \frac{h\nu c}{e} = \frac{hc}{e\lambda}.$$

Thus if $e = 4{\cdot}804 \,.\, 10^{-10}$ e.s.u.,

and $h = 6{\cdot}629 \,.\, 10^{\;27}$ erg.-sec.,

the potential required is

$$E = \frac{\nu}{8057} = \frac{12{,}412}{\lambda}.$$

In words this states that an electron which has fallen through one volt will excite a line of wavelength 12,412 A. and of wave-number 8057 cm.$^{-1}$.

Thus the ionization potential of sodium is $\dfrac{41{,}449}{8057}$ or 5·14 v.

The ionization potentials of the elements of the short periods and of homologous elements in the long periods are shown graphically in Fig. 13.

§ 38. Arc and Spark Spectra.—The lines of a spectrum cannot be usefully ordered into series until any that are due to transitions in the ionized atoms have been separated from those arising in the normal atom. This point is of no consequence in considering the alkalis, because the spectra of the alkali ions are so difficult to excite that there is little confusion ; in the alkaline-earth spectra, however, many ionic lines are almost as easily produced as lines of the normal atom, so that both occur side by side on the same photograph, and can be separated only when spectra excited under different conditions have been compared.

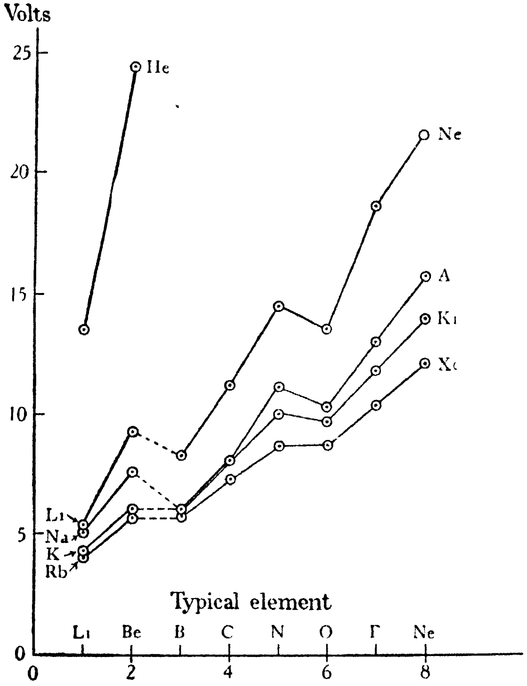

Fig. 13.—Ionization Potentials of the Elements of the Short Periods.

Lines due to the normal atom are in general easier to excite. The Bunsen flame, used in simple chemical tests, excites a few lines only ; but if the temperature of the flame is raised, by using oxy-acetylene instead of coal-gas in air, many more lines appear, and the spectrum becomes very similar to that excited by an arc. Again King, working with a high-temperature furnace, found that as the temperature is raised some lines get relatively stronger and others relatively weaker. It need hardly be said that the intensity of all lines increases with temperature, but the photographic exposure is correspondingly reduced. The lines which grow relatively weaker are lines characteristic of a flame or arc; the lines which grow relatively stronger are those characteristic of a spark (§ 28. 1). The latter are typically those arising in the ion, for when atoms are roughly handled by an electric spark many lose an electron, and any further transitions which occur must be between different states of the ion. An interesting confirmation of this interpretation is that, in an arc, lines due to the ion appear particularly strong near the negative electrode, whither the positive ions are drawn, and whence a copious stream of electrons emerges to meet them. Thus though both arc and spark excite lines arising in both atom and ion, those arising in the atom are commonly referred to as "arc lines" and those arising in the ion as "spark lines." The arc spectrum of calcium is written Ca I and the spark spectrum Ca II. (See *Frontispiece*.)

A helium spectrum characteristic of certain low-pressure stars contains series very similar to those of hydrogen, but where the hydrogen formula contains the constant R the helium formula contains the constant $4R$; these series are known to arise in the helium ion. A like similarity is observed between all spectra arising in atomic systems containing the same number of electrons; thus ionized magnesium has doublet series like those of sodium, but whereas the formula for the series of Na I is

$$\nu = T - \frac{R}{(m + a)^2},$$

the formula for the series of Mg II is

$$\nu = T - \frac{4R}{(m + a)^2},$$

while in the spectrum of doubly ionized aluminium, written Al III, the constant is $9R$. These constants have been satisfactorily explained by Bohr (Candler, 1937*a*, p. 14).

The multiplicity of a spectrum depends only on the number of electrons present; in fact, one may say quite generally that if the atom or ion has an odd number of electrons the spectrum will be of even multiplicity, while if the number of electrons is even the multiplicity will be odd. Thus the arc spectrum of calcium consists of singlets and triplets, but the spark spectrum consists of doublets just as the spectrum of potassium does. The increase in the nuclear charge, however, in passing from K I to Ca II gives all the terms greater energy, so that the term differences are greater and the lines lie farther in the violet.

No purpose would be served by describing here the more complex types of spectrum, for which the reader may refer to Chapter VI of *Spectrochemical Analysis in 1938* (Candler, 1938), or to Candler's *Atomic Spectra* (1937).

§ 39. **Raies ultimes.**—The theoretical conditions which the transition producing the *raie ultime* must satisfy are still in dispute (Candler, 1937*b*, p. 121), and to the practising spectroscopist it may well seem doubtful if theory has added anything to the knowledge laboriously accumulated by de Gramont and his followers (§§ 29, 30) ; for one thing the theoretical *raie ultime* may occur in a part of the spectrum difficult to observe and so be of little use. Certainly the most recent rule (Meggers and Scribner, 1934 and 1935) needs a more thorough grounding in theory (Candler, 1937*b*, Chapters XII and XIII) than can be given here, if it is to be understood.

§ 40. **Homologous Lines.**—If an aluminium alloy contains 4 per cent. of copper, the copper can be estimated spectroscopically with an accuracy of some 5 per cent. of its own weight ; that is, the analysis shows that the percentage of copper in the material is between 3·8 and 4·2 per cent. ; the percentage accuracy is independent of the element concerned and of the percentage actually present, provided the latter lies between 0·01 and 10 per cent.

In seeking greater accuracy one asks first the source of the error ; of the whole 5 per cent. some 1 to 1½ per cent. arises in measuring the density of the line, some 2 per cent. in irregular variation in the light-source and in the consequent variations in the relative intensities of the lines to be compared ; the remainder is due chiefly to errors of sampling, the specimen and the standard not being of uniform composition throughout (§ 161. 4).

No great improvement is to be expected in measurements of density ; the theoretical physicist has been working at the problem for more than a decade. Sampling errors can be reduced in various ways, which are still the subject of active, but more or less empirical investigations. Variation in the relative intensities of the two lines being compared can be largely avoided by adopting Gerlach's principle of the internal standard, using if possible " homologous " lines (§§ 117, 118).

One would like a source which is absolutely standard, but in both arc and spark, variations in current and voltage seem unavoidable. One compares, therefore, a line of the element being estimated with a line of another element present in known amount ; this is known as the method of the " internal standard." In works practice the internal standard is one of the lines of the major constituent of the alloy, aluminium in the above example ; but in the laboratory a trace of an element not previously present may be added. Thus when Foster and Horton (1937) wanted to estimate boron in the leaves of a plant, they took two identical specimens of the leaves ; to both they added the same quantity of gold, and to one they added a measured quantity of boron ; they then compared the intensities of a gold and a boron line in each specimen. From these relative intensities the weight of boron present in the original leaves could be calculated.

The choice of suitable lines is very laborious if tackled empirically, but if the two spectra have been analysed into terms, theory can give a clear lead. Thus Foster and Horton used the boron line 2497·7 A., which arises as ${}^2S_{\frac{1}{2}} \rightarrow {}^2P_{1\frac{1}{2}}$, and the gold line 2427·9 A., which arises as ${}^2P_{1\frac{1}{2}} \rightarrow {}^2S_{\frac{1}{2}}$. Both are arc lines, they have roughly the same wavelength, and as both end in the ground term, both require roughly the same energy to excite them ; moreover, as they lie close together the plate sensitivity will be the same for both. That they end in the ground term is unfortunate, in that it makes them liable to self-reversal, but this is less likely to occur in the spark actually used than it would have been had an arc been employed.

Since the conditions of excitation cannot be accurately controlled, the intensities of the two lines to be compared should vary in the same way as the conditions change ; for instance, an arc line of gold must not be compared with a spark line of boron. Suitable pairs of lines Gerlach (1936) calls *homologous*, and he discovers them empirically by varying the conditions of excitation widely.

Gerlach's homologous pairs have to satisfy four conditions :

(1) One line arises in the major constituent of the alloy, and the other in the minor.

(2) The wavelengths must not greatly differ, for the sensitivity

of a photographic plate varies with wavelength, and uniform development is also difficult to ensure.

(3) The relative intensity should be independent of the conditions of excitation.

(4) The lines must have roughly the same intensity when the constituents are present in the proportions actually occurring.

These conditions may conflict with one another ; when they do the more attention one pays to one, the less one pays to the other three, and so a compromise has to be sought. Thus theory can predict lines whose relative intensity will be independent of the conditions of excitation, but unless one is free to choose the standard element, as one is in the laboratory, the two will have widely different wavelengths ; moreover, the lines best satisfying this condition will normally have equal intensities only when the two elements are present in a proportion not greater than ten to one.

So valuable is the freedom in the choice of the internal standard that its introduction even into works practice deserves consideration. Thus in the above example, could the aluminium-copper alloy not be sampled hot and a known weight of silver added, or could not the alloy be re-fused with some silver ? If the silver was present to 1 per cent. as compared with the copper's 4 per cent., lines could be easily found which arise in similar transitions and satisfy all the conditions demanded of homologous lines : the 5153-A. line of Cu I and the 5209-A. line of Ag I are such a pair, both arising as $3^2D_{1\frac{1}{2}} \rightarrow 2^2P_{\frac{1}{2}}$. Experiment alone can show whether increased accuracy can be obtained, but theory certainly renders it likely. If it is, then it would still have to be set against the extra trouble involved. (See also § 119.)

If no subsidiary standard is to be introduced, and if the proportions of the two elements to be compared are predetermined by the alloy being manufactured, the final restriction on equality of wavelength leaves very little freedom for the introduction of theoretical considerations. The transitions in which the homologous pairs suggested by Gerlach arise have been listed for four different alloys, and no rule has been found to be obeyed.

Band Spectra.

§ 41 (Twyman and Allsopp, 1934). Line spectra, thus far discussed, arise from changes taking place in the atom ; in contrast, band spectra arise from changes in the molecule. Typical bands are seen if a discharge from an induction coil is passed through a tube containing nitrogen at low pressure; with low-power instruments these bands have a channelled or fluted appearance; but with high dispersion the band is seen to consist of a large number of lines lying close to one another and crowding up towards a limiting line or head.

The study of band spectra has taught us much of the structure of simple molecules; but this new knowledge is at present of theoretical rather than of practical importance. In analysis for the elements the only bands commonly used are those due to fluorine.

Reversal and Self-reversal of Spectral Lines.

§ 42. When a beam of light from a tungsten-filament lamp is passed through a sodium flame, the continuous spectrum appears with two dark lines on it; further, if the lamp is switched off, the lines formerly dark appear bright on a dark background, the positions being unaltered. In the same way the sun's spectrum is crossed by numerous dark lines, commonly referred to as Fraunhofer lines, after their discoverer.

A line seen dark on a bright background is said to be *reversed*; that such lines appear because an element absorbs the same wavelengths as it emits was demonstrated by Kirchhoff in 1860 (§ 26).

The cause and nature of this effect were well described by Kirchhoff in 1860 (§ 26). Reversal is explained by him as a natural result of his law, which may be briefly stated as follows:

"The ratio between the emission and the absorption of any body at a given angle of inclination depends upon the temperature only: this ratio is equal to the emission of a black body at the same temperature. These laws are due to Kirchhoff. They hold not only for the total intensity of emission, but also for the emission of any particular wavelength" (Drude's *Optics*, 1907, p. 499). Attention must, however, be drawn to the fact that Kirchhoff's law applies only to radiation which takes place as a result of heat, as will be appreciated by his words: "An exception can only come about with a flame in which a part of the light is produced by chemical process or with a flame that fluoresces. Experiment alone can determine whether such a flame exists."

The importance of reversal in spectrochemical analysis lies in the fact that radiation of a given wavelength, whether from a flame, arc, or spark, has to traverse a layer of relatively cold vapour of the radiating metal before being perceived by the eye or the apparatus, and reversal can take place by absorption at that wavelength by this relatively cold vapour. When the reversal arises in this way it is called *self-reversal.*

One can obtain self-reversal in a flame, preferably a high-temperature one such as that of the Méker form of Bunsen burner, plentifully supplied with a salt of sodium, for example borax, which forms a convenient bead

Self-reversal is often observed too in the following are lines: Pb 4057, Cu 3274, and Zn 2138.

Fortunately, the reason for self-reversal is so well understood that one can say which lines may and which cannot be self-reversed. The width of a spectrum line is usually determined by the Doppler effect: an atom moving towards the spectrograph appears to emit a line of higher frequency than a stationary atom, and one moving away a lower frequency; thus the width of the line increases with the velocity of the atoms, and therefore with the temperature of the source. The hot core emits a wide line, the cold outer layers absorb a narrow one, and the result is a narrow dark line down the middle of a broad bright one.

Some spectrum lines are of course wider than the Doppler effect alone would make them; these diffuse lines are due to an electric field, which produces a Stark displacement (Candler, 1937*a*, pp. 151, 158). It may well be that in the outer layers of a discharge the electric field is less than in the core, but as an electric field produces a displacement long before it splits the line, this would suggest re-absorption at one edge of the diffuse line; and this is not in fact observed Moreover, the condition for large displacements is that two terms, which are so related that the selection rules allow them to combine, have nearly the same energy (Candler, *loc cit.*), and this condition will hardly ever be satisfied in the low terms which give rise to self-reversed lines.

Of the many lines appearing in an emission spectrum only a few appear in absorption; thus in the alkalis the principal series appears in absorption, while the sharp and diffuse series do not. In the earth metals, on the other hand, the sharp and diffuse series appear in absorption and the principal series does not. The theoretical explanation is simple enough: only those lines which end in the ground term appear in absorption, for only in the ground state will there be enough atoms to absorb an appreciable proportion of the radiation passing through the vapour. The ground term of the alkalis is ^2S, and so the principal series is absorbed; the ground term of the earth metals is ^2P, and so the sharp and diffuse series are absorbed. Exceptions to this rule occur in stellar spectra, but never in the arc or spark.

The rule which applies to reversal applies also to self-reversal: only lines which arise in transitions ending in the ground term appear self-reversed ; so that when a spectrum has been analysed, one can always select for quantitative analysis lines which will not be self-reversed.

For the peak wavelength of a (relatively) broad emission line which is capable of reversal, the outer layer may often fulfil the condition for making reversal visible ; to repeat Kirchhoff's argument, if it absorbs one-quarter of the light it transmits, it emits one-quarter of the light emitted *by a black body at the same temperature*. Since the luminous part of the light-source is at a much higher temperature, it may very well be emitting much more than a black body at the temperature of the outer layer. If I_{t1} is the intensity of the emitting part of the light-source, then one-quarter of this will be absorbed. The colder outer layer of the flame will emit with an intensity of I_{t2}, but as it is at a much lower temperature this quantity will be much less than I_{t1}, and in fact may be so small as to be negligible. Thus the radiation ultimately emerging from the middle of the light-source, represented by $I_{t1}(1 - \frac{1}{4}) + I_{t2}$, may be reduced by a quarter.

In spectrochemical analysis reversal proper is of little importance, but the possibility of self-reversal must be borne in mind in all quantitative work, for when a line is self-reversed the intensity can no longer be used to estimate the percentage of the element present. An increase in the proportion of the element may even lead to a decrease in the intensity of the line as measured with a microphotometer.

Notation and Nomenclature.*

λ . . .	Wavelength *in vacuo*, expressed in Ångström units.
A. . . .	Ångström unit, 10^{-8} cm.
c . . .	Velocity of light *in vacuo*.
ν' . . .	Frequency of vibration *in vacuo*: $\nu' = c/\lambda$.
ν . . .	Wave-number in cm.$^{-1}$: $\nu = 1/\lambda$.
h . . .	Planck's radiation constant.
T . . .	Term value in cm.$^{-1}$ measured from the limit of a term sequence.

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* See also the Appendix.

$\rightarrow$ and $\leftarrow$	Denote emission and absorption: symbols for the upper and lower levels are always written to the left and right respectively of the arrows. A commoner notation uses a minus sign and places the lower level to the left.
R	Rydberg constant.
n	Effective quantum number: $T = R/n^2$.
m	Serial number.
a	Quantum defect, defined by $n = m + a$, where m is integral and a usually less than 1.
L	Orbital momentum of electrons in the atom: this quantum number is involved in selection rules.
J	Angular momentum of the atom, a second quantum number.
S, P, D, F	States of the atom in which $L = 0, 1, 2, 3$.
^2S, ^2P	The small prefix denotes the multiplicity.
$S_{\frac{1}{2}}$, $P_{1\frac{1}{2}}$	The small suffix denotes the J-value of the term.
$1S$, $2S$, $3S$	Successive terms of the sharp sequence; the number is usually the value of the serial number m.
Limit of series	Given by the vanishing of the second term of the Rydberg equation.
Term	One of the terms of the Rydberg equation for the series.
Quanta	The discrete amounts in which energy appears to be emitted and absorbed.
Stationary states	Orbits in which an electron in an atom can remain for an appreciable time.
Quantum relation	The connection between the frequency of the radiation emitted or absorbed and the change of energy involved.
"*Sharp*" *series*	Composed of lines which appear sharp under magnification.
"*Diffuse*" *series*	Composed of lines which appear diffuse.
"*Principal*" *series*	Composed of intense lines liable to self-reversal.
"*Fundamental*" *series*	The fourth type of series associated with the atom.
Selection rules	Rules which predict whether or not a given transition will result in emission of a line.

Sequence .	A succession of terms corresponding to *S*, *P*, *D*, etc.
"Odd" and "even" terms	Required by selection rules: explanation beyond scope of present elementary account.
Multiplet .	A number of lines due to one electronic transition in an atom.
Ionization potential	The energy expressed as voltage acting on the electron which is required to remove it from the atom.
Resonance potential	The corresponding energy required to cause the emission of a single line.
Multiplicity .	The number of lines emitted owing to one electronic transition.

CHAPTER III.

SPECTROGRAPHS AND ACCESSORY APPARATUS.

§ 43. The instruments and apparatus are described in this chapter as types only. Up-to-date and reliable details of construction can best be had from the manufacturers, some of whom are mentioned in § 56.

Visual Spectrometer.

For visual spectrochemical analysis the wavelength form is convenient, and very much useful work can be done with it. The forms made by most manufacturers closely follow in their dispersion the one designed by me in 1904. If alloy steels are being dealt with as well as other metals, the larger size of instrument made by several manufacturers is desirable.

Specialized instruments have been designed for use in metal warehouses, rolling mills, melting houses or scrap yards They enable any intelligent lad to estimate by simple inspection any of the metals customarily used for alloy steels with a quantitative accuracy sufficient for sorting and checking. Some makers have introduced photometric arrangements to enable quantitative estimations to be made, sometimes to an accuracy of 5 per cent. of the constituent determined.

For Bunsen flame spectra, the Kirchhoff and Bunsen type of spectroscope, made by very many firms, suffices.

Spectrographs.

§ 44. G. R. Harrison in an article on "Practical Possibilities in Spectrographic Analysis" (1936) says :

"*Use of the Diffraction Grating.*

"A statement frequently found in the literature, especially that published abroad, is that the diffraction grating cannot be used for spectrographic analysis, since it is fragile, wastes most of the light falling on it, and has ghost lines which mix with the real lines and cause incorrect results. The man who first made that statement really believed it, but it gets more amazing year by year as the number of analyses made with grating instruments increases. As to fragility, most of the first gratings ruled back in the 1880's are still in use, and a number of metallurgical laboratories, including that of the Watertown Arsenal, use grating instruments exclusively. As to wastefulness of light, even the standard type of quartz spectrograph utilizes less than 1/10,000 of the light emitted by the source being studied, and very seldom do the exposures taken with a grating require more than 60 seconds.

" In fact, with ordinary sources and with prism instruments, it is sometimes desirable to artificially lengthen the time of exposure in order to have a more truly representative burning time for the source. Only in extreme cases is the greater brightness of the prism over the grating of importance. Some of the new aluminium-coated gratings are surprisingly fast. A large high dispersion grating which I have recently tested throws 60 per cent. of its light into one spectrum, and gives good exposures in two seconds.

" As to the ghosts or spurious lines—in most modern gratings these have been reduced in intensity to the point where they do not even register photographically except in over-exposures to strong lines. Even if a grating has ghosts of intensity greater than 2 per cent. of the main line, which is an unusually high ratio, it can often be used, since the greater dispersion of the grating instrument over the prism instrument gives greater separation of the lines, and they can usually be distinguished from the lines in which one is interested.

" *Why Grating Spectrographs are used Less Often.*

" The reason grating spectrographs are used less often than prism spectrographs is very simple—there are comparatively few gratings, and it has not been found possible to turn them out at will like prisms. From 50,000 to 200,000 parallel lines from 1/15,000 to 1/30,000 of an inch apart must be ruled on a mirror, each at an equal distance from its predecessor.

" The greatest problem to be solved has been a metallurgical one, to obtain a metal which can be accurately figured and polished, like glass, and at the same time does not wear out the diamond ruling tool too rapidly. Speculum metal has been used largely in the past, but recently great strides have been made by figuring a glass mirror, evaporating a coating of chromium on this, and then on this a coating of aluminium. The ruling is done in the soft aluminium surface, which gradually protects itself with a thin transparent film of oxide, giving a brilliant reflecting surface for all wavelengths.

"As mentioned above the concave diffraction grating can be used in any region of the spectrum. When used with an auxiliary mirror and illuminated with parallel light, it gives stigmatic images like those of a prism spectrograph, and it has the advantage of a practically uniform wavelength scale, rather than one which is crowded at the red end and sparse at the short-wave end. Grating spectrographs are now being put out commercially, and as the number of gratings available increases, so that commercial manufacturers can rely on a source of supply, and the amount of optically useful crystal quartz diminishes, we can expect the grating to increase in use. Most persons who have used both grating and prism instruments prefer the grating for spectrographic analysis."

I differ from this conclusion, for the reasons stated *below*, but that is all the more reason why I quote the above passage and the following one at length, for Harrison, with a long experience with the great battery of spectrographs which he has available at the Massachusetts Institute of Technology, is probably in a better position for forming a judgment on the point than any other academic authority in the world.

Further on Harrison, after dealing with the physical side of the question of the production of radiation, continues :

§ 45. "We have seen above that difficulty of excitation (high voltage electrons required) goes with shortness of wavelength of the lines. The gases are difficult to detect spectrographically in the ordinary way not only because they are hard to excite, but also because their principal spectrum lines lie in the region of wavelength shorter than 2000 Ångstroms. This region has been studied extensively in scientific laboratories, and there it is usual to find lines of carbon, oxygen, etc., appearing in almost all spectrum photographs, so that they are relatively as sensitive as sodium is in ordinary work. While the vacuum methods needed are not now practical for industrial work, they could be made so if need arises.

" *Analyses for Sulphur and Selenium.*

" Sulphur and selenium analyses are very important and are rather difficult to carry out with chemical wet methods. Two years ago Merrill and the writer undertook a series of experiments which showed that sulphur and selenium could both be handled quite well by means of the spectrograph. As soon as we looked into the theoretical reasons which showed why sulphur and selenium show 'no *raies ultimes* or sensitive lines' as given in the tables, it was possible to suggest four different ways of handling these two elements. Three were of the type now practicable only in the research laboratory, but the fourth gives promise of being useful generally.

" It is possible, on theoretical grounds, to predict in advance which of the spectrum lines of an element will be most sensitive, and usually also to predict where in the spectrum these lines will be found, if they are not known. A study of the data indicated that sulphur and selenium should both have sensitive lines, but that these all lie at wavelengths shorter than 2100A., which is the lower limit of most quartz spectrographs. For sulphur the three lines which should be most sensitive are between 1807 and 1826A., while for selenium they are between 1960 and 2062A. In short, the standard type of quartz spectrograph does not quite reach them, both because of the absorption of its quartz optical train, and because of the absorption of light of these wavelengths by the oxygen in the air. Also we must overcome the natural disadvantage at which sulphur and selenium find themselves in metallic alloys due to their high excitation potentials, which are above the ionization potentials of many of the metals.

" The second difficulty can be overcome by using arcs with very high current, or sparks with high average excitation. We have overcome the first by flushing out the sealed spectrograph continuously with a stream of commercial tank nitrogen, allowing this to leak out through the slit against the arc or spark placed directly in front of it. If a lithium fluoride prism or diffraction grating can be used instead of the usual quartz prism, so much the better.

" We have successfully analyzed for sulphur down to the lowest concentrations which we could obtain analyzed chemically in nickel, steel, and other materials.

" The standard methods of determining the relative concentrations of atoms from the intensities of the lines on the plate are adequate and have been repeatedly discussed in the literature. The rotating sector disk is probably the most convenient method of varying the light intensity by known amounts, with some simple form of microphotometer or its equivalent to measure the line densities.

"If investigations of the type outlined above continue to be carried out at the rate at which they are now progressing in various laboratories, we should have available shortly convenient and accurate methods for analyzing spectrographically any chemical substance."

With this passage I agree ; but I should consider a small fluorite vacuum spectrograph a more suitable instrument for the purpose than a grating spectrograph.

Let it be said at once that grating spectrographs are almost indispensable for many physical investigations. That they are not likely, in my opinion, to come into wide use for analysis in industrial laboratories is due to the following reasons :

§ 46. Disadvantages of Grating Spectrographs for Spectrochemical Analysis and Absorption Spectrophotometry.—(1) Ghosts of strong lines may be mistaken for lines due to impurities. Although this is not a great drawback in an academic laboratory, it is very objectionable in an industrial laboratory.

(2) Owing to the fact that there are second and higher orders of spectra (although in *some* gratings these are very much reduced in intensity, they still exist), there is a very serious danger that a strong spectrum line in the second order may be mistaken for a weak one in the first order.

(3) The grating spectrograph is astigmatic, and cannot, therefore, be conveniently used with the logarithmic-sector, stepped-sector, stepped-plate, stepped-slit, or other similar quantitative methods. Further, owing to the astigmatism the grating spectrograph cannot conveniently be used to examine the variation of the spectrum from pole to pole of the electrodes, which is often of importance in spectrochemical analysis. These objections are removed by using the stigmatic arrangement, which is among the forms of grating spectrographs made. This instrument, however, has the objection of being very bulky.

(4) The extension of the range of the spectrograph into the vacuum region demands vacuum apparatus and technique, the former very expensive, and the latter requiring great skill and experience. Further, not only must the spectrograph be evacuated (or filled with nitrogen), but the space between the light-source

and spectrograph also, a necessity which could not be tolerated in routine industrial analysis.

(5) The world supply of gratings is quite inadequate to fill the demand even of one single manufacturer. Further, they are not priced on an economic basis. If they were, their use for industrial purposes would almost certainly be precluded by their price.

At the present date about 95 per cent. of those writing about spectrochemical analysis use the quartz spectrograph.

Choice of Spectrograph.

§ 47. Having decided, as we presume he will, on the quartz spectrograph, the beginner will next have to decide which size of instrument to use. The various makers are mostly in accord in offering for such work two sizes, one of which is usually called the "Medium Quartz Spectrograph," and the other the "Large Quartz Spectrograph," following the names given by me to these sizes when I designed the instruments from which all modern quartz spectrographs for metallurgical work are derived (Pollok and Leonard, 1907).

For most work with non-ferrous metals (for example, the detection and estimation of impurities in brass, zinc, lead, copper, aluminium, magnesium, tin, gold, etc.) the medium size has ample dispersion, and has the advantage over the large that the whole spectrum is obtained on a single plate, on which a scale of wavelengths can be photographed. Where the spectrum of the main substance is very complex, the large spectrograph is required. The full spectrum in the large instrument extends over four plates, usually 10 in. long, but a sufficient range of distinctive lines can often be photographed on one plate, while the change-over from one spectral position to the other is very easily performed.

For the analysis and detection of certain metals, notably the alkali-metal group, it is desirable to have at one's disposal a higher dispersion in the visible region than is given by the ordinary quartz system, and some spectrographs are provided with optical systems of highly dispersive glass, which can be substituted for those of quartz. A large quartz spectrograph is made fitted with both kinds of optical train.

As a guide to the selection of a suitable quartz spectrograph the following lists have been compiled of elements whose spectra are so complex that the large instrument is necessary when impurities are to be detected in them.

TABLE IV.—USE OF LARGE SPECTROGRAPH.

Metals for which the Large Spectrograph is Necessary.		Metals for which the Large Spectrograph is Desirable, but not Essential.	
Chromium,	Titanium,	Manganese,	Platinum Group,
Cobalt,	Tungsten,	Thorium,	Nickel Alloys.
Iron,	Uranium,	Vanadium,	
Molybdenum,	Zirconium.		

It should be observed that in most cases where metals other than the above are being tested for the presence or absence of the above metals, the medium quartz spectrograph has sufficient dispersion for the work, as the number of spectrum lines corresponding to these metals when they are present only in minute quantities is generally not excessive.

For the routine examination of some elements in steel alloys (*e.g.* nickel, chromium, and silicon) it has been found that the dispersion of the medium-size instrument is sufficient; but for other elements the larger dispersion is to be preferred in order to obviate the risk of lines of such elements being obscured by those of iron. Again, unsuspected elements (which may be a source of trouble in an alloy) are sometimes overlooked when the medium instrument is used, whereas this does not happen with the large one.

The larger instrument has a further advantage: for quantitative work using the microphotometer it is always advisable to work with as wide a spectrograph slit as possible (even 0·1 mm. is not too large), and this is impossible with a complex steel alloy on the medium instrument, since the lines would overlap. The reason for the use of a wide slit is to overcome errors due to grain of the plate, and this is important in the use of the microphotometer.

The ease with which lines can be detected (without high magnification of the plate) and the need at times for a complete analysis of a material lead the author definitely to recommend the use of the larger instrument for steels and all the metals referred to in Table IV. Its value has already been proved in a number of commercial laboratories.

Two other sizes, which we may call the "Intermediate" and "Small" spectrographs, are both capable of useful work within the scope of their dispersion. The small size was used by Brownsdon and van Someren in the routine works analysis of brass for the determination of lead, tin, iron, nickel, aluminium, and manganese

(§ 180), and in similar analyses of lead and lead alloys for tin, antimony, cadmium, arsenic, bismuth, copper, zinc, and silver (§ 207); the intermediate size is suitable for soil analysis by the flame method of Lundegårdh.

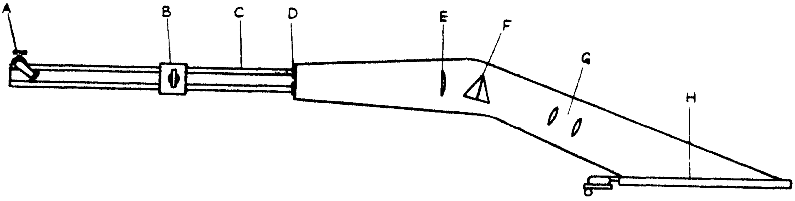
Smith also has used a small spectrograph for the assay of ternary lead alloys, such as are used for cable-sheathing, etc. Smith has also used it for the determination of cadmium, lead, and iron in zinc to conform to the limits of the British Standards Institution specifications (§ 207).

The dispersions from 2,000 to 8,000 A. of these four instruments are approximately as follow:

Large quartz spectrograph	67 cm.
Medium quartz spectrograph	22 cm.
Intermediate quartz spectrograph	14 cm.
Small quartz spectrograph	7·5 cm.

The Medium Quartz Spectrograph.

§ 48. The medium quartz spectrograph consists of a slit *D*, collimating lens *E*, whose function is to make the rays more or less parallel so that they all fall on the prism *F* at approximately the same angle of incidence, the quartz prism and the camera lens *G*, and photographic plate *H*; these parts will now be considered separately.



A Arc or spark stand.
B Condensing lens.
C Bar for accessories.
D Slit.
E Collimator lens.
F Quartz prism.
G Camera lens.
H Photographic plate.

Fig. 14.—Typical Design of a Medium Quartz Spectrograph.

The Slit.—The slit *D* is an extremely important part of the instrument. We have already seen what a great deal of information Fraunhofer was able to obtain as compared with previous observers of the sun spectrum, merely on account of the fact that he used a narrow slit, the width of which subtended a very small visual angle at the prism. This was why he observed the Fraunhofer lines in such richness of detail. When it is remembered that 0·01 mm. is a quite usual width of slit to use for metallurgical work, and that variations along the length of the slit may be unpleasantly perceptible in the spectrum and, with some methods of working, a source of serious error, it will be realized what very fine mechanical finish has to be put into the jaws of the slit.

The purpose of the slit of a spectroscope is to form a very narrow aperture through which, no matter how narrow it may be, light can pass from the exterior of the spectroscope to every part of the object glass of the collimator.

It will be seen from Fig. 15 that if the jaws of the slit are flat surfaces, then even if the jaws are comparatively thin it will be impossible when the slit is nearly closed for rays of light to reach all parts of the object glass. Thus, no rays diverging more than the ones shown as *R R* and *S S* can reach the object glass, with the consequence that only the portion from *R* to *S* is used. Under these circumstances, neither the definition nor the amount of light is the best that can be obtained.

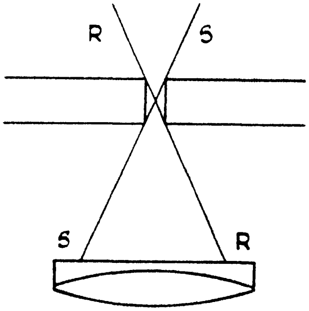


Fig. 15.

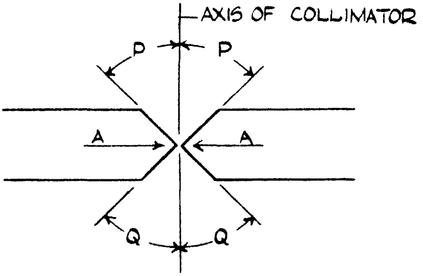


Fig. 16.

What is desirable is obviously that the edges of the jaws should be sharp, as shown at *A A* in Fig. 16, and that the clearance angles both in front of and behind the slit *P P*, *Q Q* should be great enough to allow the passage of oblique rays.

In practice it is found that a convenient angle for *R S* (Fig. 15) is 90°, and if this is equally divided, so that *P*, *P*, *Q*, *Q* (Fig. 16) are all equal to 45°, there is no obstruction to the rays of light.

It will also be seen that it is very necessary for the edges *A A* to be exactly opposite to each other, or, strictly speaking, in the same plane perpendicular to the axis of the collimator. Otherwise, if these edges are approached they may assume some such position as shown in Fig. 17. In this case light will reach only a portion of the collimator, the two edges will not be in focus at the same time, and the definition will be quite unsatisfactory. It is necessary that the edges should be exactly opposite not only at one point of the slit jaw, but of course along the whole length of the slit.

To examine a slit, it should be held up towards a light, say a window, at arm's length ; it should then be tilted from side to side. There should be a clear passage of the light when the slit is tilted through a very large angle, demonstrating that it is free from the error shown in Fig. 15. The cutting off of light when being tilted through a large angle should be equal on both sides, indicating that the slit is free from the error shown in Fig. 17, and the light should be uniform throughout the whole length of slit, even when it is tilted to an angle.

The fineness of grain of the edge is best observed on an actual spectroscope with sodium or mercury light, a condenser, and a very fine slit.

It is customary nowadays to supply a slit opening bilaterally. The present writer resisted this movement for many years, since he believed, and still believes, it to be entirely unnecessary for analytical work. There are few manufacturers who can solve successfully the problem of making a slit which complies with the above-mentioned necessary conditions and at the same time retains these conditions while opening symmetrically. However, the practice is now universal with all better-class spectrographs, and the best makers have successfully solved the mechanical difficulties involved.

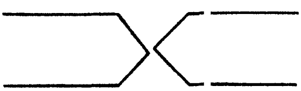


Fig. 17.

There should be a shutter for giving the exposure, and it is convenient for this to be within the slit, so that the jaws are always visible.

Slit Width.—There are two conflicting desiderata concerning width of slit, resolution of near lines and intensity of each line, between which a compromise must be made, and it is interesting to see how far this is effected in a particular case.

The focal aperture which for a number of reasons is frequently chosen for spectrometers and spectographs is of the order of $f/10$. The "normal slit" according to Schuster (1905) for such an instrument is $10\ \lambda = 0{\cdot}005$ mm. for the green of the visible spectrum. A slit width of 0·02 mm., therefore, corresponds to a "slit factor" of 4, and from Schuster's table we find that the intensity of a fine line is 3·15 times that for a " normal slit " and 77·4 per cent. of that of an infinitely wide slit. It would appear, therefore, that for an instrument of this aperture ratio a slit width of 0·02 mm. is about as good a compromise as could be made for ordinary spectrography.

§ 49. The Prism.—The prism requires to be made of two halves, one of right- and one of left-rotation quartz, since quartz is doubly refractive even for rays passing along the axis. The two halves of the prism require to be accurately cut so that the rays pass along the axis of the quartz crystal, and, following the procedure introduced by the present writer, they are now generally put together in optical contact (Twyman, 1905).

§ 50. The Lenses.—The camera lens requires to be a compound lens consisting of two or sometimes three separate lenses, depending upon circumstances and the conditions which have to be fulfilled. In the computation of the systems of spectrographs the advantages and disadvantages of the two- and three-lens systems depend to a great extent on whether the computer is at liberty to assume the use of non-spherical surfaces in the system, for this provides the computer with an additional device for correcting the aberrations. The better-class spectrographs take full advantage of this. The production of non-spherical surfaces calls for special methods of manufacture and high accuracy of working. Both collimator and camera lens may have aspherical surfaces.

The collimating lens is in most standard instruments made of crystalline quartz, not achromatically corrected. There are two reasons for this, one being that satisfactory materials to use in conjunction with quartz for annulling the achromatic aberration are not available. Fluorspar, the optical properties of which are admirable for the purpose, is very rarely obtainable in pieces which are sufficiently large, clear, and homogeneous. Other materials which might be used in spectrographs are lithium fluoride and rocksalt (protected between two quartz lenses). Fused quartz is another possible material, but it is rarely available in sufficient size and homogeneity to be employed. Other materials available in the requisite size fail either by being too strongly doubly refracting, or by having too small a transmission in some part of the spectrum.

The other reason is that, as will be seen in Fig. 14, the result of having non-achromatized lenses is to reduce the focus towards the ultra-violet, so that the photographic plate is tilted at a fairly large angle relative to the pencils of light falling on it. This effectively increases the dispersion of the instrument, and if the lens system were achromatized so that the spectrum would be formed on a plane at right-angles to the axis of the camera, it would be necessary to make the instrument considerably larger were it to have the same dispersion. It is true that the optical " resolving power " of a lens system depends only on the aperture, but there is a limit to the detail which can be reproduced on the photographic plate. Thus, although the image formed on a photographic plate by an achromatized system would possess all the detail of that of the more dispersed spectrum, that detail could not be faithfully reproduced on the photographic plate with the dimensions of spectrograph which are generally adopted for this kind of work.

Focussing is usually provided for the collimator and camera lens, but this is not always done. The maker is possibly divided between his desire that the user should not inadvertently throw the focus out of adjustment (which he may be unable or too impatient to reproduce exactly), and his desire that the user should be able to correct the adjustment if it should become faulty in transit or otherwise. Even differences of temperature may sometimes produce observable variations of definition.

§ 51. The Plateholder.—The plateholder fits in a slide in which it can be moved vertically so that a number of spectra can be taken on one plate. It is possible, if one wishes, to take forty or more photographs on one plate.

Seeing that with a good optical system a change of focus of 0·1 mm. can be detected, it is obvious that the plateholder and its slide must be accurately made. As we shall see when we come to consider the examination of the spectra, it is a great convenience that each spectrum line should, in a series of photographs, always be on the same straight line. Not only does this imply that the slide should be accurate, but that the photographic plate should be flat, or if not flat of the same curvature in each horizontal plane, a condition none too easy to fulfil. Preferably, of course, the optical system should be so designed and made that a perfectly flat plate can be used—photographic plates of ordinary thickness could then be used without risk of breakage.

Some makers supply a wavelength scale so mounted that it can be brought into contact with the photographic plate by means of a small lamp, which is illuminated for about a second. The wavelength scale is impressed on the photographic plate and develops up with the spectrogram. This is very convenient for obtaining rapidly knowledge of the wavelengths of various parts of the photographed spectrum and for finding any desired lines, but it is not, nor is it intended to be, accurate enough to measure the wavelengths of spectrum lines with the precision necessary for identification of a doubtful line; neither the dispersion of spectrographs nor the position of the spectrum on the photographic plate is absolutely invariable. Considerable temperature variations affect both of these.

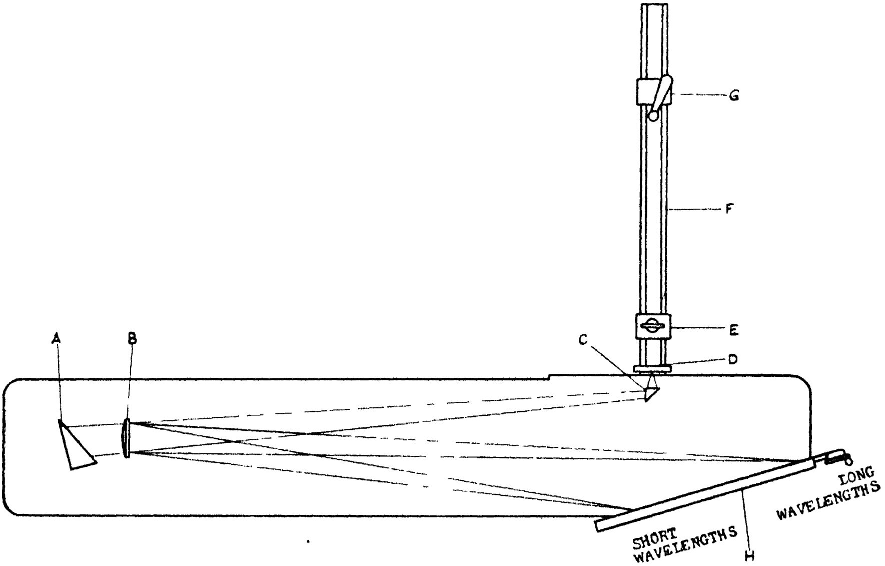
Spectrographs nowadays are supplied in a permanently adjusted position, but the makers issue, or will provide if asked, instructions for re-adjusting them should that be necessary. Users may be advised, however, that they should not attack the adjustment of their instruments too readily; it may well be that the adjustment at the end of their endeavours may be no better than at the beginning. Some makers send out a specimen plate taken with the actual instrument, and when this is available the user would be well advised not to re-adjust his instrument unless it is giving a definition inferior to that of the standard plate. Even then it would be better for him to send a photograph to the maker, who may be able to tell by inspection what, if anything, has gone wrong with the instrument.

The Large Quartz Spectrograph.

§ 52. The size of instrument usually called the "Large Quartz Spectrograph" has a focal length of approximately 170 cms., about three times that of the medium-size instrument, but the reader is warned that occasionally the size here referred to as "medium" has been described by one or two makers as "large." It is obvious that if the construction of this instrument were made of the same nature as that of the medium size, it would be excessively long and awkward in shape, something like 14 or 15 feet long in fact, and for this reason it is made, following the instrument designed by the present writer about 1910, of the Littrow form shown in Fig. 18.

Slit and plateholder are the same as in the Medium Quartz Spectrograph, but the prism needs to be only a 30° quartz prism, from the second surface of which the light is reflected. There is one drawback to this form of instrument, namely, that the light reflected from the two surfaces of the quartz lens is reflected back in sufficient quantity to produce a certain amount of diffused light on the photographic plate, unless means are taken to avoid it. It is easy to make the lens of such shape that the reflected light is collected into one, or at the most two, images formed between the photographic plate and the lens, which images can be blocked out by interposing a small obstruction in the body of the instrument. Unfortunately, however, to adopt this procedure precludes one from utilizing the best form of surfaces for definition. Makers avoid this difficulty in various ways, on which it would be invidious for the present writer to express an opinion.

In some modern instruments the rotation of prism, focussing of lens, and tilting of plateholder are all made automatically by turning a single drum, which records the range of spectrum recorded on the photographic plate.



A Prism.
B Lens.
C Reflecting prism.
D Slit.
E Condensing lens.
F Bar for accessories.
G Arc and spark stand.
H Photographic plate.

Fig. 18. - Typical Design of Large Quartz Spectrograph.

Four ranges of spectrum are required fully to cover the total length of spectrum as the dispersion of this instrument is so great, but for industrial work three ranges ordinarily suffice.

Another form of large quartz spectrograph, which may find some favour, particularly among those concerned with the analysis of steels, has a glass and quartz train which are made interchangeable by the turning of a handle, the glass train giving nearly three times the dispersion of the quartz for the visible part of the spectrum.

§ 53. The Electrode Holder.—The means of excitation of the flame, arc, or spark will be dealt with in Chapter V.

The electrode holder consists of two insulated clamps adjustably mounted, but within this simple statement room has been found for a great diversity of forms. Not only has each maker a different idea of the best form to market, but a considerable proportion of those writing on spectrochemical analysis have designed electrode holders to suit their individual requirements.*

Some of these variants which originate in the necessities of a special technique will be mentioned later in describing the ways of exciting the radiation. For arc or spark work with solid metals the chief requirements are that the apparatus should be robust, and should have rack and pinion *E* and *F* (Fig. 19) for separating the electrodes. To this may be added with advantage a separate rack and pinion *A* and *B* for adjusting the pair of electrodes in height without altering their separation, a device first used by A. de Gramont, after whom such a holder is called a " Gramont " stand (1918). Finally, there should be some convenient means of adjusting the pair of electrodes horizontally. Such a stand is shown diagrammatically in Fig. 19.

Condensing and Positioning Lenses.

§ 54. Condensing lenses, used between the light-source and the slit of a spectrograph, are of two kinds :

(*a*) spherical lenses (bi-convex or plano-convex) ;
(*b*) cylindrical or sphero-cylindrical lenses.

Spherical lenses may be of two kinds, the one forming a real image of the light-source on the slit, and the other forming an image of the light-source on or near the collimator lens of the spectrograph.

When a sphero-cylindrical lens is used with the cylinder axis vertical, a vertical band of light will be projected on to the slit; when the axis of the cylinder is used horizontally, then a horizontal image of the light-source will be formed on the slit.

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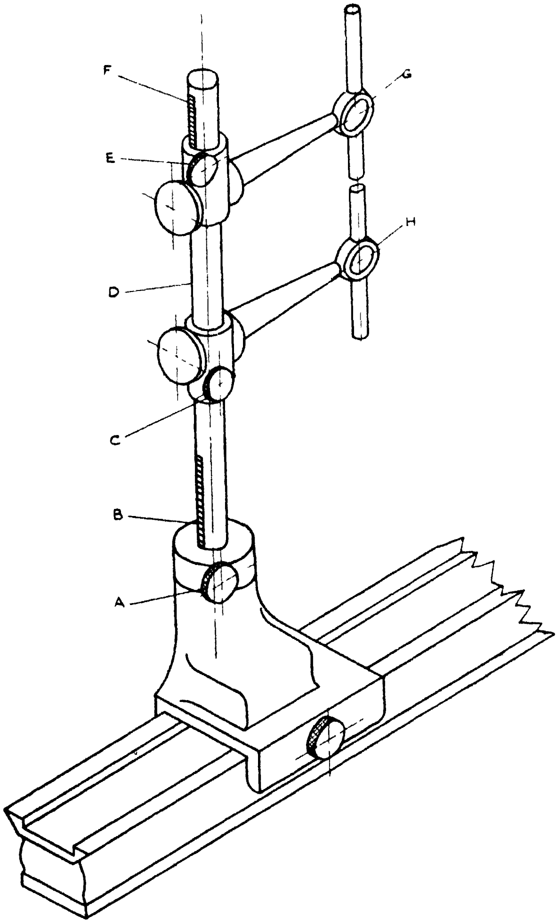
* Gatterer (1939) compares many types.

Uses.—(*i*) *For forming an image on the slit.* It may be desired that the spectrum should indicate the radiations which are present at each point between the poles of the light-source, and in this case



A, B	Rack-and-pinion raising and lowering adjustment.
C	Clamp for sliding adjustment of lower arm.
D	Main column.
E, F	Rack-and-pinion adjustment for length of arc.
G, H	Electrode clamps.

Fig. 19.—Typical Arc and Spark Stand (de Gramont).

an image of the light-source must be formed on the slit. This mode of illumination enabled Lockyer many years ago to observe the "long" and "short" spectrum lines (§ 28. 1), and it is used as a means of selecting the middle portion of the iron arc when the latter is used to determine standard wavelengths (Twyman and Smith, 1931, pp. 14 and 15).

The spherical condenser used in this way is occasionally of considerable use in spectrochemical analysis : one example is that of the selection of suitable line pairs for comparison. The radiation from the middle of an arc emanates chiefly from the neutral (unionized) atom, and produces the flame and arc lines. On the other hand, owing to the greater potential gradient near the electrodes, radiations arising from the ionized atom are emitted there, and the lines so produced are termed "spark lines" (§ 38). In quantitative spectrochemical analysis it is usual to compare arc lines of the base substance with arc lines of the alloying element, and spark lines with spark lines ; a pair of lines so chosen is called a "homologous" line pair and is not likely to vary much in relative intensity with alterations in the excitation conditions (§ 40).

When an image of the source is focussed on the slit, the beam of light passing through the slit fully illuminates the whole aperture of the collimator lens (or lenses) of the spectrograph. The condensing lens is usually employed thus in spectrochemical analysis either for a general search for all the elements contained in a substance, or for projecting the radiation from a selected part of the source—such as the negative electrode—into the spectrograph.

(*ii*) *For obtaining uniform intensity along the whole length of each spectrum line with light from the whole light-source.* In quantitative analysis where the density of the spectrum lines is to be measured by a photometric instrument it is essential that the lines should be of uniform density along their whole length, and it is usual to adopt a system in which the length of the slit is uniformly illuminated by radiation from the whole of the light-source.

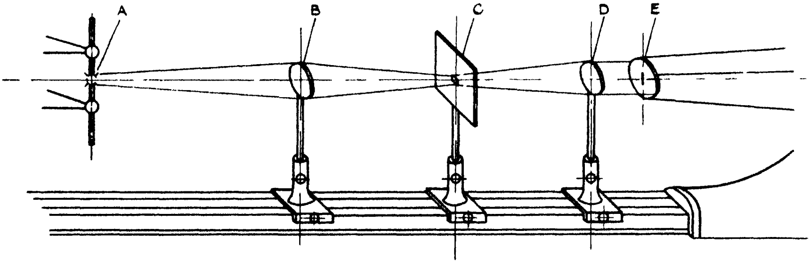
The condensing lens for this purpose must be of such diameter and focal length, and so disposed between the light-source and slit, that the whole beam of light passing through the slit would, without any obstruction, form a real image at the collimating lens of the spectrograph. The lens must be appropriately designed for use with the particular spectrograph.

Less light passes through the slit with this form of illumination ; consequently exposures must be increased to obtain equal density of spectrum.

(*iii*) *Sphero-cylindrical lenses.* Sphero-cylindrical condensing lenses have been considerably used in the past both for general spectroscopic work and for spectrochemical analysis.

In early days the sphero-cylindrical lens was used to form a vertical line of light on the slit. This way of using it has now been abandoned, but recently such lenses have sometimes been used to form a *horizontal* line of light on the slit. Small movements of the arc away from the optical axis do not then affect the illumination. Here again the lens should be designed specially for the spectrograph with which it is to be used, and the maker should state the position of light-source and lens.

(*iv*) *Combined use of two lenses.* It has already been shown that for uniformity of intensity along the spectrum lines a spherical lens forming a real image inside the spectrograph must be used.



A Light-source.
B First condensing lens.
C Diaphragm and screen.
D Second condensing lens.
E Slit of spectrograph.

Fig. 20.—Combined Use of Lenses for uniformly illuminating Slit from Selected Portion of Light-source.

On occasions (as for the cathode-layer method) it may be desired to secure this condition using only the radiation from a small selected region of the light-source. In this case the light from the source *A* (Fig. 20) must be first projected by a spherical lens *B* on to a screen *C* in which is mounted a variable aperture. This aperture, which may vary from 1 to 4 mm. in diameter, is then treated as the light-source. By altering the height of the light-source the light passing through the aperture can be chosen from any desired part between the electrodes. An image of the aperture is then formed on the prism of the spectrograph by a condensing lens *D* placed near the slit *E*, when a uniformly illuminated line will be received on the photographic plate.

(*v*) *Mirror and lens system.* As a variation of the above two-lens system, a concave mirror may be used in place of the first lens, preferably aluminized (not rhodium-plated or silvered) on the front surface.

The ideal condensing lens would be achromatic ; but in practice this would entail the use of quartz-fluorspar or quartz-rocksalt combinations, which are too expensive. Achromatism is attained by the use of the concave mirror, but this is rarely employed in practice.

§ 55. **Positioning Lenses.**—When using condensing lenses to form an image on the slit it is easy to ensure alignment of the light-source, but when using a lens to get uniform illumination in manner (*ii*), only a circle of light is formed on the slit, and alignment of the light-source is difficult. This is an important point, for if alignment is bad, the image formed inside the spectrograph may possibly not fall wholly within the aperture of the collimator lens, and the photograph will, of course, reproduce only the radiation from the part of the image which does so, thus leading to erroneous conclusions. For this reason a " positioning " lens is useful to form an image on a screen, the latter being engraved with a fiducial mark to indicate when the light-source is in correct alignment.

All the above types of lens except the positioning lens need to be of quartz ; they should be designed appropriately for the type of spectrograph they are to be used with ; and their proper positions should be given by the maker.

§ 56. **Principal Makers of Spectrographs and Accessories for Metallurgical Analysis.**—The following is a list of the principal makers of spectrographs :

Great Britain.

Adam Hilger, Ltd., 98 St. Pancras Way, Camden Road, London, N.W. 1 (grating and prism spectrographs).
Bellingham & Stanley, Ltd., 71 Hornsey Rise, London, N. 19.

France.

Jobin et Yvon, 26 rue Berthollet, Arceuil, Seine.
Huet (Société Générale d'Optique), Paris.

Germany.

R. Fuess, Berlin-Steglitz, Düntherstr. 8.
Steinheil, München 8, St. Martinstr. 76.
Carl Zeiss, Jena.

U.S.A.

Bausch & Lomb Optical Co., Rochester, N.Y.
The Gaertner Scientific Corporation, 1201 Wrightwood Avenue, Chicago.
Applied Research Laboratories, 1208 San Julian Street, Los Angeles, California (grating spectrographs).
The Baird Associates, 20 Palmer Street, Cambridge, Mass. (grating spectrographs).

CHAPTER IV.

THE MICROPHOTOMETER.

Principles of the Microphotometry of Spectrograms.

§ 57. The microphotometer is a photo-electric or thermo-electric device for measuring the blackening of any small area on a photographic plate. The instrument was first used to determine the relative intensities of the spectral lines from photographs of stellar spectra.

The first microphotometers were recording instruments in which the whole spectrum or a selected range was traversed, and a photographic record taken of the deflections of the galvanometer. For spectrochemical analysis a non-recording form is generally used, for it is both quicker and much less expensive.

Fig. 21 is an illustration of a typical form of the instrument. *M* is the light-source, a 6-volt 18-watt motor headlamp, with directly soldered connections, running from a source of constant voltage. A prism at *H* deflects the beam at right-angles on to a 25-mm. microscope objective *G* below the stages *E* and *F* ; this forms an image of the filament of the lamp on the plate, which is placed film side uppermost in the frame *F*. A second objective *A* forms an image of the plate on the symmetrical slit *S*, the jaws of which are in white metal and form a projection screen on which the spectrum is seen under a magnification of × 10. Behind the slit *S* is mounted a photo-electric cell *N* of the rectifier type. At *L* and *K* are two lenses, one spherical, *L*, and one cylindrical, *K*, which can be pushed into the beam as required ; we shall refer to *L* as the "viewing lens."

The slit *S* may be a symmetrically opening one, controlled by a knurled ring *P* of large diameter. It should have a protective hood *R* to keep out stray light.

The frame *F*, in which the plate rests, is supported on a carriage *E*, which runs freely on guides *I* and *J*. The operator can move the carriage quickly by hand in the direction of its length in order to scan from one end of the plate to the other The plate can also be accurately traversed by a screw adjustment, which facilitates setting the plate in its correct position, or making accurate micrometric measurements of the distance between lines, as described *below*

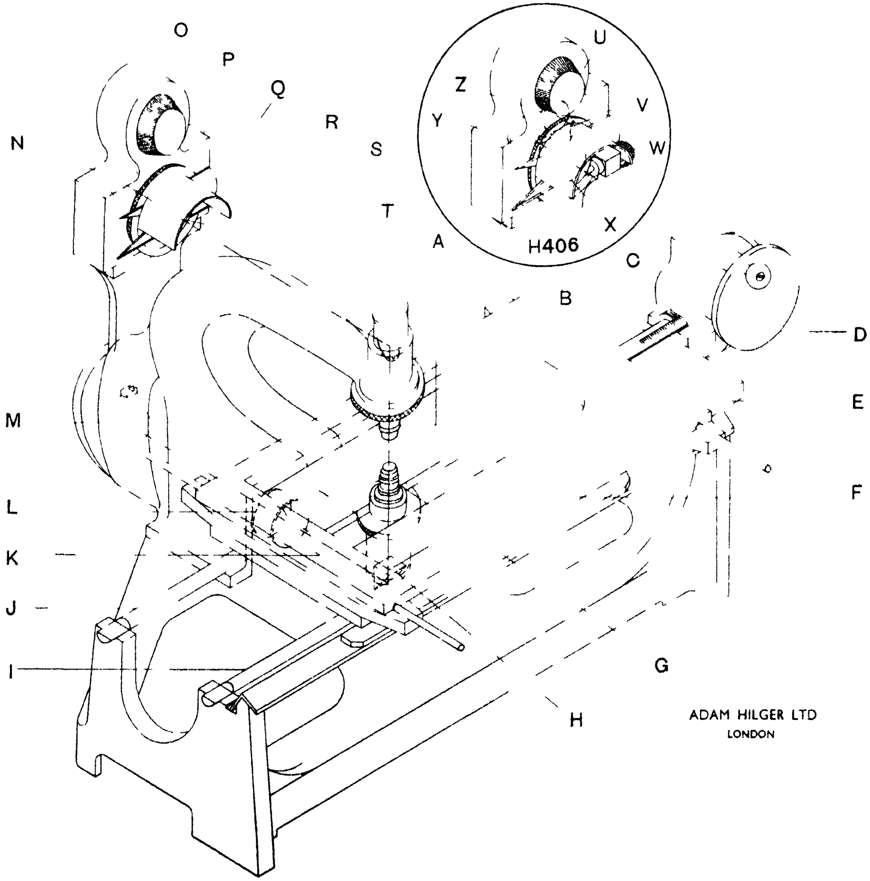


Fig 21 —Typical Form of Microphotometer

This screw motion is further provided with a fine slow-motion C', consisting of a worm gearing. By means of this the operator traverses the plate at a suitable rate (say, two turns of the control handle *D* per second), about ten seconds at this rate sufficing to traverse a given spectrum line across the slit of the microphotometer. This rate should enable the galvanometer to acquire the deflection corresponding at each point to the blackening of the line being traversed.

The frame *F* is also movable relative to the carriage in a direction parallel to the length of the spectrum lines, to permit movement from one spectrum to another.

§ 58. Taking Readings.—In order to take readings the plate is placed in the frame *F* with the emulsion side upwards. The viewing lens *L* is brought into position, and the plate then becomes illuminated by a small area of light, instead of by an image of the filament, so that on the slit *S* appears a projected image of the spectrum under examination. The stage can be accurately set, with the mechanical adjustment provided, until the image of the required line falls parallel to the slit, and the plate can then be traversed by means of the screw *B* until the line falls slightly to one side of the slit.

The plate having thus been carefully set in position, the viewing lens *L* is displaced. This has the effect of focussing the light from the filament on the slit to form an image of the filament ; although the line cannot now be seen, it is still imaged on the screen, as the objective *T* has not been moved, and very much more light falls on the photocell than during the setting process. The handle *D* of the fine-slow motion is slowly rotated so that the image of the line passes across the slit. The minimum reading of the galvanometer is noted. The amount of light transmitted by the spectrum line under examination is then shown by the difference between this minimum reading and the reading when the light is excluded from the photocell.

Normally, during a reading, the length of spectrum line illuminated is about 0·7 mm. This is often the maximum length of illumination that can be allowed, but it is advantageous to illuminate a greater length if possible, as the effects of grain in the emulsion, dust on the plate, and similar disturbing factors are reduced. To render this possible, in a mount near the viewing lens a cylindrical lens *K* can be interposed of such focal length that the length of line illuminated is 2 mm. In taking a reading using this length of illumination, then, the only difference from the procedure outlined *above* is that, before the galvanometer deflections are observed, this lens should be turned into the beam. If it is desired that the length of illumination of the line shall be only 0·7 mm., then the cylindrical-lens mount is turned so as to leave the beam clear.

The method of measuring the light transmitted is extremely simple if a rectifier type of photocell is used : the sensitivity of the latter is so large that a galvanometer can be used to measure the current it gives ; and it has the further advantage that no battery is required. Another advantage of the rectifier cell is that it responds almost solely to visible radiations ; therefore the ordinary commercial objectives are suitable for the optical system. Most of the response of the most sensitive types of emission cell is due to short infra-red radiation ; when they are used special objectives are needed, as those of the ordinary type are not sufficiently corrected for this region to give good definition.

Use of the Microphotometer in Quantitative Analysis.

§ 59. In its essentials quantitative spectrochemical analysis resolves itself into the correlation of the relative intensities of certain lines in a spectrum with the percentages of the elements producing these lines. These relative intensities are difficult to determine directly (*i.e.* by direct measurement on the source *), and the fact that most spectra are recorded photographically seems to lend itself to an easy solution. Unfortunately, the blackening of the photographic plate is a most complicated phenomenon, the two most important characteristics of which, from the viewpoint under consideration, are (1) that the blackening at any wavelength is not a simple function of the exposure, and (2) that this blackening function varies with wavelength.

If reliable intensity measurements are to be made covering any considerable range of wavelengths, then, in addition to the exposure of the spectrum under investigation, an exposure must be made to some standard source whose intensity variation with wavelength is known. In this manner the variation of plate characteristics with wavelength can be allowed for. Sometimes, however, two wavelengths under examination are very close to one another. In this case the wavelength calibration can be omitted, provided it is remembered that an uncertainty has been introduced. Whilst this calibration can be omitted if approximate results only are desired, the second calibration necessary, that of blackening against exposure, can *not* be omitted. Any " short " method which proposes this should be regarded with suspicion. The opinion of those who have made this their special study is that it is only by putting upon each plate an intensity calibration that accurate and consistent analyses can be made.

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* Except in the visual region.

§ 60. The principles of the method of spectrophotometry worked out by the astrophysicists are very clearly described by Dobson, Griffith and Harrison (1926). They say :

" The density of a photographic image depends not only on the exposure it has received, but also to a great extent on the time, temperature, etc. of development. In practice it is not feasible to make the development of all plates so nearly alike that the density of the image alone can be used as a measure of the intensity of the light falling on different plates. Further, even if development could be carried out with sufficient uniformity, one would be asking a great deal of the plate-maker if one demanded that all plates of the same make should have identical properties. Moreover it is well known that certain characteristics, such as the rate of development of a plate, change with the age of the plate.

" For such reasons it is necessary to use the photographic plate to make a comparison of the intensities of two or more beams of light which give images on the same plate. The only strictly accurate method of procedure is to find positions on two images on the same plate where the densities are identical. Then, provided the times of exposure were the same, and the wavelengths of the lights employed identical, we may with confidence assume that the light incident on the plate was of the same intensity in the two cases, provided that the sensitivity and the development were uniform all over the plate.

" This is a fundamental principle in all trustworthy photographic photometry, and though in certain cases it is not possible to adhere to it strictly (as will be seen below) every modification introduces at the same time possible sources of error.

" Photographic photometry has to be applied to all kinds of problems, but one of two general methods of working will be found applicable in nearly every case. Where we are measuring the intensities of various beams of light, it is convenient to allow the light to illuminate uniformly an optical wedge, an image of which is thrown on the plate. If two such images are formed by the two beams which have to be compared (the wavelengths being the same) we shall have two images, each changing in density along its length. By means of a photometer we can then find places on the two images where the densities are equal, and can measure the difference in distance of these points from the reference line on the wedge. From this, knowing the wedge constant, we can at once find the ratio of the intensities of the two beams.

" In certain cases it is necessary to make the results obtained from a number of plates all comparable with one another. In this case some source of light must be provided, which will remain accurately constant over the whole set of experiments, and an image obtained by means of this source must be formed on each plate, to be used as a standard for comparison.

" It must be specially noted that no method of photographic photometry without a special calibration of the plates * can give the relative intensities of two beams of light of different wavelengths, since the characteristics of the plates often differ considerably for different wavelengths. Where such a comparison is necessary it is best made by the aid of photographs of the spectrum of a source which radiates as a ' black ' or ' grey ' body of known temperature, so that the ratio of the energies in the various wavelengths can be calculated.† "

Properties of Photographic Plates.

§ 61. Symbols used in this Section.—I_1 and I_2 represent the maximum intensities of radiation of two spectral lines which are to be compared.

B represents the density of the corresponding blackened image in the developed photographic plate as defined by Hurter and Driffield (1890) : namely, if i_0 is the intensity of radiation allowed to fall on the blackest part of the photographed line, and i the intensity of the radiation transmitted, then

$$B = \log_{10} \frac{i_0}{i}.$$

In measuring the absorption of liquids, etc. by spectrophotometry, the word " density " comes into frequent use to describe the absorption of the liquid under examination, and to avoid confusion resulting from the use of the word "density" to denote both log I_0/I for the liquid and log i_0/i for the photographic plate, it is convenient to call log i_0/i the "density of blackening," or for short just "blackening," and the word is used in this sense in this book. The word in use in German is *Schwarzung*.

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* " It is not always safe to assume that the calibration obtained with one batch of plates will apply accurately to another batch of the same make, nor even to other plates of the same batch if kept for any length of time."

† " An arc between carbon electrodes, or even the hollow crater of the positive electrode, does not strictly radiate as a ' black ' or as a ' grey ' body. In its spectrum, lines and bands due to impurities and the surrounding atmosphere may be observed ; the spectral intensities in the regions immediately adjacent to these lines obviously do not obey the ' black body ' law of radiation. In general, however, isolated portions of the spectrum can be obtained which may be regarded as due to radiation from a black or a grey body, and these are sufficiently extended to enable accurate measurements to be made."

§ 62. Photographic Plates.—The photographic plate in metallurgical spectrochemical analysis is used, of course, to record the position of lines, but it does more than this. Properly dealt with, it enables variations in the intensity of a line to be measured with an accuracy which at its best may be well within ± 2 per cent. in a single measurement.

If the spectroscopist carries out the procedures laid down in Chapter IX, he will get the accuracies there promised; but if he wishes to acquire competence in dealing efficiently with any problem, he must know something about the properties of photographic plates.

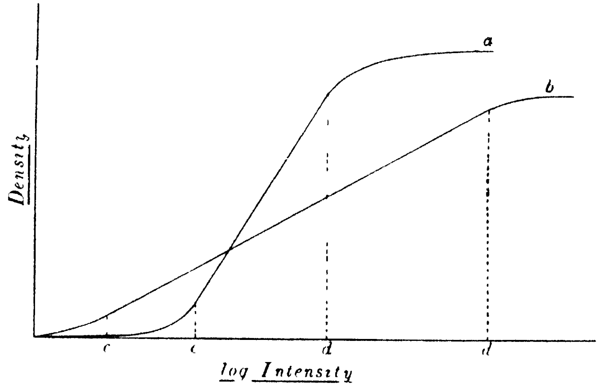

Fig. 22.

It has long been known that, for neighbouring areas of a photographic plate and for a constant time of exposure, the density of blackening of the developed plate is related to the logarithm of the intensity I of the light causing that blackening in the way shown by the curves of Fig. 22.

The ratio of the increase of blackening to the increase of the logarithm of light intensity (*i.e.* the slope of the curve) is greatest on the straight portion of the curve, where it is specially denoted by the symbol γ. Thus, in making photometric measurements, a plate and method of development (which latter is also very important) giving a large gamma (γ) are desirable, as in *a*, Fig. 22.

On the straight portion of the curve the smallest detectable change in log I is obviously given by the smallest detectable difference in blackening divided by γ.

With a large gamma the range of correct exposure (given by the straight portion *c d*, Fig. 22) is small, so that if a plate of large gamma be used one must adjust the exposure of the parts of the spectrum where measurements are made in accordance with the spectral distribution of the light-source and the sensitivity of the emulsion to different wavelengths, in such a way that one is working on the portion *c d* of the curve.

For preliminary surveys one will require a plate with a large latitude $c'd'$, Fig. 22, that is, a plate with a small gamma. In this case, however, the values of I determined will be less accurate, since a given error in measuring B will imply a larger corresponding error in I.

The use of the microphotometer in spectrochemical analysis is to determine $B_1 - B_2$, the difference of blackening of two lines to be compared, and from this can be found I_1/I_2, which can be used to determine the relative percentages of two constituents S_1 and S_2 of the substance being analysed.

§ **62.1. Processing.**—It would be very useful to compare the choice of plates and the processing methods preferred by various workers. Vincent and Sawyer (1939) in a paper on the rapid processing of plates draw attention to two important points :

(i) " If the time is quite short, of the order of one minute or less, uniform development is hardly to be anticipated with random or no agitation of the solution ; under such conditions, the Eberhard effect may be quite troublesome. Uniform positive agitation not only minimizes these difficulties, but has the desirable effect of hastening all phases of the processing, developing, hardening and fixing.

(ii) " The cost of the solutions is very moderate and the use of fresh baths of standard activity promotes uniformity in processing. The use of solutions to complete exhaustion is never justified, and, indeed, they should be replaced at the first evidence of fatigue."

The following passages from two manufacturers of photographic plates are of interest. They are replies to a request for advice on securing uniformity in processing :

Messrs. Kodak, Ltd., Wealdstone, Middlesex.—" The essential factor in securing uniformity of development over a plate is violent surface agitation during development, which may be obtained by : (1) vigorous rocking in a dish ; or (2) brush development with a soft camel-hair brush ; this method may, however, cause minute surface scratches, which will be a disadvantage in microspectrographic work. A useful method to avoid this is to move a glass rod backwards and forwards over the plate, about 1 mm. above the surface.

"The following papers on standard development may be of interest to you :

(1) 'Standardization of Plate Testing Methods. Standard Development,' W. Clark, 1925, *Photographic J.*, **65,** 76-89.
(2) 'Sensitivity Variation of X-ray Photographic Films,' W. H. George, 1937, *Proc. Phys. Soc.*, **49,** 357-363.
(3) 'Dispositif pour le Développement sémi-automatique des Plaques en Sensitométrie,' S. E. Sheppard, R. H. Lambert and G. Atkins, 1935, *Proc. 9th International Congress of Photography.*"

Messrs. Ilford, Ltd., Ilford, Essex.—"With either the thin film or the process plates it is customary to use a hydroquinone caustic developer and to develop right out. This is by far the easiest technique, since the possibility of variation in development over the plate surface is reduced to a minimum. It is only when one is developing to something less than the maximum contrast which the plate can give that the control of development becomes critical. If the contrast obtained with the caustic developer is too great it would be necessary for you to use an M.Q. formula and to arrange matters so that every part of the plate receives exactly the same treatment in the processing baths. This is best brought about by brush development. The method employed is to place the developing dish in a thermostatically controlled water tank at 65° F. [18·3° C.]. The developer to be used is put into a convenient vessel and brought to the same temperature. The plate is then laid in the dish, emulsion side upwards, and the developer is steadily poured over it, plenty of developer being used. The plate is well brushed during development in two directions at right angles with a flat, long-haired, soft brush, slightly wider than the plate. This brushing is continued for the whole time of development. The developer is then poured off and replaced with a stop-bath of 1 per cent. metabisulphite.

"Even with a uniformly developed plate it is a very easy matter to introduce inequalities by subsequent treatment, particularly in the drying process. Here again, for accurate repetition work it has been found necessary to adopt a standard technique."

§ 63. Application of these Principles.—The principles described *above* have been adapted by a number of workers to spectrochemical analysis, a variety of methods being used to obtain the calibrating radiations. Duffendack (1933) used a slit which had varying widths in known steps, Breckpot (1937*a*) a stepped sector rotating in front of the slit, Harrison (1929) and Follett (1936) a platinized plate of stepped densities, all of them with good results. Duffendack, for example, working with liquids, obtained an accuracy of 1 to 2 per cent., a result the excellency of which is partly to be attributed to the perfect homogeneity of the substance (liquid). Lundegårdh, who did not calibrate his plates in the sense now in question, but also working with solutions, got a like accuracy by careful standardization of the photographic conditions and reference to standard solutions (for methods employed to calibrate the plates see §§ 129, 136, 137, 138).

An industrial laboratory, dealing as it does with a range of alloys requiring analytical control, offers ideal facilities for collecting specimens of accurately known composition which can be used as standards for the production of graphs, and it is by the use of these standards that the plate calibration is carried out by most workers to-day.

Lomakin (1930) in the optical laboratory of the Bureau of Weights and Measures, Leningrad, used as early as 1930 a method based on microphotometer measurement of the lines of the constituents, involving calibration of the plate by use of "standard specimens." He used an arc between the specimens to obtain a spectrum, and investigated the effects of arc voltage and time of exposure on the results. His method is very similar in principle to that most widely used now in metallurgy.

A number of subsequent workers with the microphotometer, some calibrating the plate by means of stepped spectra, some by the use of standard specimens, adopted numerous variations of technique. Still earlier references will be found in the paper by Scheibe, Linström and Schnettler (1931): "Ein Verfahren zur Steigerung der Genauigkeit in der quantitativen Emissionsspektralanalyse und seine Prüfung." In this paper is described a method (Scheibe and Schnettler's) very similar to Lomakin's, but in which the plate characteristic is determined by means of two lines of the main metal; a method which does not seem to have received the attention it deserves.

§ 63. 1. Comparison between the Stepped-spectrum (Duffendack) and Standard-specimen (Lomakin) Methods.—Probably most workers use methods based on Lomakin's, and it is this, in the form described in §§ 68 and 69, which is at the present time generally employed in my laboratory, because it is very simple and practical. I do not remember having seen any attempt made to compare the accuracies of the two methods on theoretical grounds, and therefore offer the following brief account :

In the stepped-spectrum technique the operations are :

(i) Taking a spectrum of the unknown specimen.

(ii) Taking on the same plate a stepped spectrum of a comparison light-source, in which we know without any uncertainty that the logarithms of the intensities of illumination of successive steps are a, $a + b$, $a + 2b$, $a + 3b$, ...

(iii) Measuring the blackening of one line of the basis metal and that of a neighbouring one of the metal to be determined.

(iv) Measuring the blackening of each step of the stepped spectrum in the neighbourhood of the same line, and from the results plotting a graph of B against log I. The shape of the working portion of this curve is independent of the absolute intensity of the comparison light-source.

(v) Reading from this curve $\log I_c - \log I_b$ ($= \log I_c/I_b$), corresponding to $B_c - B_b$,

where I_c is the intensity of the line of the constituent being determined ;
B_c is the blackening of the line of the constituent metal ;
I_b is the intensity of the line of the basis metal ;
B_b is the blackening of the line of the basis metal.

Hence the percentage of the constituent metal can be read from a graph previously prepared by carrying out like operations on a series of known specimens.

In the method which we may call Lomakin's, in the form detailed in §§ 68 and 69, the operations are the same except that in place of one stepped spectrum (operation ii, *above*), one takes several spectra of known specimens. This operation, therefore, is not free in Lomakin's method from any vagaries arising from the particular way in which the spark may be behaving.

The same consideration applies also to the operations involved in drawing the graphs.

One must conclude, therefore, that a somewhat higher degree of consistency may be expected from adopting a stepped-spectrum routine.

§ 63. 2. It appears, however, that there is a particular way of treating the measurements that renders the results more independent of variations of exposure and development, and of the type of plate used, than any other, and this will now be described. The method is rapid. The spectra of twenty or more specimens can be taken on one plate, and the whole process of exposures, developing, fixing, washing, and drying can be compressed within forty minutes, while the measurement for each line can in routine work be carried out on the microphotometer within twenty seconds, providing an instrument of the non-recording type be used.* It is not surprising, therefore, that it has been found easily possible for a single observer to do thirty analyses a day for five minor constituents.

No novelty is claimed for the routine prescribed here, except for selecting, checking, and simplifying the methods of the above and other workers.

§ 64. Routine recommended.—Quantitative spectrochemical analysis depends on the assumption that the ratio of intensities of two lines emitted respectively by the major and minor constituents of a homogeneous substance is determined uniquely by the composition of the latter, providing the method of excitation of the lines is fixed. The assumption is sound within certain limitations which have been established by experience. In practice a reliable technique can always be found. If then the ratio of such intensities on a number of specimens of a particular type of alloy of differing known contents be measured, it is possible to plot a graph by means of which an analysis of an unknown specimen of a similar alloy can be made by repeating the process.

Although there are instances where a direct measurement of intensities—visually (Twyman, 1931) or by a photocell (Lundegårdh, 1934, p. 104)—has advantage for a particular analysis, especially when it has to be repeated very frequently, it is customary to take photographs of the spectra, in which case the ratio of the intensities of the radiations has to be deduced from the blackening of their developed images on the photographic plate.

§ 65. Photometry of the Photographed Lines : Plotting Graphs.—Owing to the well-known characteristic of the photographic plate whereby in the under- and over-exposed parts of the plate changes of the exposure produce little change in the blackening, under- and over-exposure of the lines to be measured must be avoided. It is therefore best to keep to a blackening of not less than 0·2 or 0·3 for the weakest line, and not more than 1·0 for the strongest. To ensure this it is sometimes necessary to use different exposures for each constituent which is to be determined. By adopting the simple procedure of plotting galvanometer deflections obtained on the microphotometer against the percentage of the constituent, serious discrepancies between the results may be obtained with differences of photographic plate or development technique, and this procedure is therefore to be avoided.

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* By adopting modern methods of rapid processing of the plates the development, etc. can be greatly accelerated (§ 62. 1).

§ 66. Theory of the Method recommended.—Suppose that in a compound homogeneous substance, consisting of a main constituent A and a minor constituent a it is desired to find the percentage of the minor constituent relative to that of the major one. Let the intensities of the selected lines of the major and minor constituents be I_1 and I_2, the galvanometer deflections obtained with the microphotometer D_1 and D_2, the maximum blackenings of the lines on the photographic plate B_1 and B_2, and the time of exposure E.

The blackening * B of a given photographic plate developed in a given way produced by an intensity of illumination I, in time E, is closely expressed by the formula †

$$B = \gamma \log (IE^p) - a, \tag{1}$$

where p, γ, and a are approximately constant. Applying this to the two lines in question,

$$B_1 = \gamma \log (I_1E^p) - a, \text{ and } B_2 = \gamma \log (I_2E^p) - a, \tag{2}$$

whence

$$B_1 - B_2 = \gamma \log \frac{I_1}{I_2}. \tag{2a}$$

$B_1 - B_2$ is therefore an expression independent of exposure and of every characteristic of the photographic plate except its gamma.

Now the galvanometer deflection ‡ D is proportional to the fraction of light transmitted by the spectrum line under examination, and for a given intensity of light incident on the plate

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* See definition, § 61.

† Provided that neither of the lines is over-exposed or under-exposed (§ 65).

‡ The deflection is the difference between the reading for the line and the zero reading obtained when the light beam of the microphotometer is cut off.

$$B_1 = c - \log D_1 \text{ and } B_2 = c - \log D_2, \tag{3}$$

where c is a constant ; whence

$$B_1 - B_2 = \log \frac{D_2}{D_1}. \tag{4}$$

From (2a) and (4)

$$\log \frac{I_1}{I_2} = \frac{1}{\gamma} \log \frac{D_2}{D_1}, \tag{5}$$

and this also is independent of the exposure.

Now I_1/I_2 varies regularly with the percentage composition. If, then, the logarithms of the ratios of galvanometer deflections be plotted against the logarithms of the ratios of the known percentages there will result a graph which—within the limits stated—is independent of the exposure. The graph will not be independent of γ, but a change in this will merely have the effect of changing all values of log D_2/D_1 by a constant factor. This factor can be determined from the standard exposures on the plate and applied to all the specimens to be determined. Without logarithmic plotting in this way, such simple correction is not possible, and this is regarded by the present author as a very important feature of the technique adopted. For the purpose of this correction it is necessary to plot values of only D_2/D_1 logarithmically, whilst the percentage composition can be plotted on any scale. But if both co-ordinates are plotted logarithmically the graphs will in many cases be straight lines, and this is an obvious advantage in drawing the curve (Twyman and Harvey, 1932).

§ 67. Effect of Continuous Background.—In addition to the line spectrum the spark gives a background of continuous spectrum, and in measuring a line we are really measuring line *plus* background. It is not possible to correct for this in any simple manner, and it has always been a source of difficulty (Strock, 1936) ; it is therefore important to reduce the intensity of this background as far as possible by suitable arrangement of the sparking conditions (*e.g.* by varying the amount of inductance in the circuit). The effect of the residual background may be seen from the following analysis :

Suppose that the intensities of the background emission are

i_1, i_2 superimposed on the line intensities I_1, I_2 considered *above* ; then equation (2*a*) will become

$$\begin{aligned} B_1 - B_2 &= \gamma \log \frac{I_1 + i_1}{I_2 + i_2} \\ &= \gamma \log \frac{I_1 (1 + i_1/I_1)}{I_2 (1 + i_2/I_2)} \\ &= \gamma \log \frac{I_1}{I_2}\left(1 + \frac{i_1}{I_1} - \frac{i_2}{I_2}\right) \qquad (2b) \end{aligned}$$

(neglecting powers of i/I). This means that the shape of the calibration curve will be modified by and will depend on the relative intensity of the background spectrum. If the intensity of the background changes independently of that of the lines, it will lead to errors in the determination. Actually, however, under the sparking conditions recommended *below*, small variations in the background intensity do not cause significant errors.

If the slit width is changed the relative intensity of the continuous background will be altered, so that a constant slit width is an important part of the method. It is not difficult to set the slit to the same width with sufficient accuracy. This importance of a constant slit width in eliminating background is not always realized. Its effect has, however, been carefully analysed by Follett (1936), who showed that greater accuracy is obtained by using a constant and fairly narrow slit. It will be noted that the method of correction for variation of plate gamma (γ) is not affected by these considerations.

Gamma of the Plate.—There is one important consideration in the choice of photographic plates quite apart from the question of grain, sensitivity, and so forth. It will have been noticed that the sensitivity of the photographic method depends on the gamma (γ) of the plate, and is greater for a large gamma. On the other hand, for a plate with a large gamma the range of exposure which will give a satisfactory result is smaller, so that it becomes necessary to adjust the exposure for the line intensities that are being measured more carefully, in order that neither of them may be under- or over-exposed. The range of density referred to *above* (0·3 to 1·0) applies to plates of fairly large gamma, although it must be remembered that all plates show decreasing gamma-values for decreasing wavelengths.

The theoretical principles of the method having been set out, the way is now clear to prescribe what may be called a standard method of taking and treating the measurements in quantitative spectrochemical analysis : firstly to prepare reference graphs, and secondly to utilize them in determining the percentage of a minor constituent of a substance relative to the percentage of the main constituent.

The adjective "standard" is applied to this routine not to claim it as superior to the numerous other routines differing from it by much or by little ; but merely as a convenient term of reference for the purposes of this book.

§ 68. Routine to be adopted.—(1) The same method of producing the arc or spark as was used in preparing the graphs should always be employed for the analysis—*i.e.* same shape of the ends of the electrodes, same distance between their points, same electrical circuits, etc. Small departures can perhaps be allowed, but the degree of laxity permissible can be found only by experience, and it is desirable to start by being over-careful rather than the contrary. It is best of course also to use the same type of photographic plate and the same developer and developing routine.

(2) Lines of the major and minor constituents which are not too far apart should be selected. It is desirable also to select lines the relative intensity of which does not vary with changing electrical conditions. This seriously restricts the choice of lines, and if lines cannot be found to fulfil this condition the electrical conditions must be all the more carefully controlled.

(3) A series of photographs is taken on one and the same plate of alloys of known composition in which the various constituents vary over the range of percentage which is of interest. Several photographs should be taken of each of these standards.

(4) Readings of the galvanometer deflections are taken in the way to be described later, and the results for each of the constituents recorded in four columns : alloy No., D_1 (for main line), D_2 (for constituent line), D_2/D_1, and the percentage q of constituent. The results are plotted on a graph with values of $\log D_2/D_1$ as abscissæ and of $\log q$ as ordinates.*

(5) The specimens to be analysed are dealt with as in (3) and (4), the percentage being found from the graph.

(6) Spectra of two or three of the standard alloys of known composition are included on each plate in order to see whether

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* Instead of taking logarithms, logarithmic paper can be used.

their measurements accord with the graphs.* If they do not, by reason of a different photographic plate or development technique having been adopted, a correction is easily applied (see § 66). Other errors, such as accidental displacement of the spark, local irregularities of the plate, etc., cannot be corrected in this way, but will usually be revealed if repeat exposures are made.

If in plotting the graphs some of the results show constant disagreement with the chemical analyses (points coming off the curve), the chemical analyses may be suspected; if varying inconsistencies are found, segregation is probably present in the specimen.

Application to a Specific Analysis.

§ 69. Details are given in Chapter IX as to the size of spectrograph, length of exposure, etc. suitable for various metals and alloys, etc. With appropriate alterations the use of the microphotometer is much the same for all alloys, and indeed all substances, and has already been described *above* in general terms.

There are few cases of spectrographic analysis where advantage cannot be taken of previous experience in determining the best forms of the electrodes; which is to be preferred: the flame, the arc, or the spark; which are the best lines to select; the best presparking times and exposure; and so forth, and information on these points is to be found by reference to Chapters VIII and IX.

Photographic Technique.—Suitable plates are Ilford Ordinary, and they should be developed in a standard metol-quinol developer, washed, and fixed rapidly in an acid hypo bath, washed, and dried. If the drying is done by rinsing in alcohol and placing in a current of warm air the whole process need not take more than ten minutes. It is essential that the plate be free from dirt and stains of any description.

Much more rapid processing of the plates is possible; see § 62. 1.

Length of Slit.—A suitable length of slit is 2·5 mm.

Microphotometer.—The plate of standards, after drying, should be placed in position on the frame of the microphotometer. Suppose the graph is being prepared for the determination of copper in duralumin. The best lines to use for this purpose are Al 2322 and Cu 2247. The plate-holder slide is moved along so that the aluminium line 2322 is near the photocell slit. For this adjustment a rapid movement of the slide can be used. Now, moving the slide very slowly (a specially slow screw adjustment is desirable for this), the minimum deflection for the aluminium line is measured. The reading of the minimum deflection for the copper line 2247 is then taken in the same way.

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* Preferably several spectra of each standard; these provide for checking the calibration of the plate.

This procedure should now be repeated for all the exposures of these lines on the plate, and the mean of the minimum deflections taken for the line pairs of all the photographs of each standard specimen. The object of this is to average out any accidental variations in the spark.

The ratio of the average deflection of the copper line to that of the aluminium line is taken with a slide-rule. The logarithms of these ratios should now be plotted as abscissæ against the logarithms of the percentage contents as ordinates.

To use the graph, the specimens to be analysed should be spectrographed in the same way (the more on the one plate the better). At least two standard samples, the one containing the alloying elements near the upper-limit specification, and the other near the lower limit, must be photographed on the same plate as the specimen to be analysed. Where possible a third sample, in which the content of the minor element is about midway between the upper and lower limits, should be included.

Graphical Plate Calculator (*Owens*, 1938*a*).—This instrument was developed to increase the speed of analysis by reducing to a simple graphical operation the conversion of spectral line blackenings, obtained with a microphotometer, into percentage concentrations of the element under analysis. The chief advantages of the apparatus lie in the economy of time and the diminished probability of arithmetical error. Both are achieved by the great simplification in the arithmetical portion of the conversion.

The calculator proper consists of a drawing-board bearing a sensitometry curve for the plate being used, and is equipped with a parallel straight edge constrained to move only in a direction perpendicular to its length, and carrying a scale of concentrations.

Dealing first with the spectra of the standard samples, it is ascertained whether the logarithms of the ratios of the deflections give the correct percentages on the graph. If they do, the percentages of the unknown specimens can be read off the graph. If not, the logarithms of the ratios of their deflections must be multiplied by the same factor as is required to correct the logarithms of the ratios of the standard samples before applying to the graph to read off the percentage compositions.

Desiderata in Microphotometers for Spectrochemical Work.

§ 70. (1) In routine analysis it is a great help, not only to speed but also to accuracy, to be able to take a large number of spectrograms on one photographic plate. In such a case the spectrum lines are necessarily short. Provision should therefore be made to restrict the length of line under examination to 1 mm. It should not be much less than that, or the grain of the plate may become an important source of error. Indeed, Sawyer (1939) considers that the area of plate utilized should be not less than 3 to 5 mm. in length and 25 to 50 μ. wide. However, in an investigation on the effect of grain-size ancillary to his paper on the use of the microphotometer, Follett (1936) adopted a slit length corresponding to 0·75 mm. on the plate, and found that in five independent measurements of the relative intensities of two lines the probable error of a single observation, calculated from the residuals, was 1·3 per cent.

(2) If such a short length of line is measured on an accurate microphotometer, it is found that the grain of the plate begins to come into operation and gives slightly differing measurements if different parts of the line are measured. This may be corrected by the inclusion of an astigmatic lens, so that the density measured is the average of that of the whole length of line illuminated.

(3) It is necessary to traverse the line slowly, in order that the galvanometer may attain the deflection corresponding with the maximum density of the line. A specially slow motion is therefore desirable, so designed that if the observer rotates this at anything from, say, one-half to two revolutions per second, he can be sure that the correct deflection is obtained without the necessity of paying meticulous attention to the rate at which he turns.

(4) It frequently happens, particularly in special analyses, that the identity of a faint line may be in doubt. In such a case it becomes necessary to determine its wavelength accurately. This is done by interpolation between neighbouring lines about which there is no uncertainty. By the addition of a reading microscope to the microphotometer accurate measurements of

wavelength by interpolation can be made by means of the screw which is an integral part of the apparatus.

(5) It is important that the manipulation of the plate (tilting it, bringing the desired lines into position, moving rapidly from one spectrum to another) should be easy and convenient. Speed in working depends very much on this.

(6) It is not always appreciated how important a factor in the accurate measurements of the microphotometer is the accurate focussing of the lines. Commercial photographic plates are sometimes not flat enough for one to move to different parts of the plates and still retain sufficient accuracy of focus for the best results. Focussing by eye, unless done very carefully, is not sufficiently good. In those microphotometers which have a separate movable lens for focussing the line on the photocell slit the focussing can be done with great rapidity and exactness by the parallax effect caused by a lateral movement of a lens in a suitable part of the light path.

(7) The microphotometer must be workable with a slit of fineness appropriate to the very finest lines to be measured.

Determination of Wavelengths by Interpolation.

§ 71. If an iron comparison is used simple linear interpolation will give all the accuracy required for identification of unknown lines, except in the following short gaps :

2115 to 2126 A., 2211 to 2228 A., 2423 to 2438 A.,

while if an iron-chromium alloy is used there will be ample provision of lines even for these three narrow regions.

An iron arc enlargement marked in standard wavelengths will be found very useful in this connection.

Review of Published Work on Spectrochemical Analysis with the Microphotometer.

§ 71. 1. A comprehensive review of published work on spectrochemical analysis with the microphotometer has been published by the British Non-ferrous Metals Research Association (Smith, 1939). The subject-matter is as follows :

' *Practice of Various Workers as to*

(1) Size and shape of the electrodes.
(2) The presparking period.

(3) Illumination of the spectrograph.
(4) Blackening curves of the photographic plate.
(5) Interpretation of density measurements.
(6) Calibration of the photographic plate.
(7) Stepped-wedge and stepped-sector methods :

  (*a*) stepped-wedge methods ;
  (*b*) stepped-sector methods.

(8) Three-line method.
(9) Corrections for variable conditions.
(10) Choice of line pairs for measurement.
(11) Spectrum background.
(12) Effects due to alloying constituents.
(13) Effect of crystal structure and metallurgical condition.
(14) Industrial application of the method.

Summary of Published Procedures.

(1) Aluminium alloys.
(2) Copper alloys.
(3) Lead alloys.
(4) Magnesium alloys.
(5) Nickel alloys.
(6) Tin alloys.
(7) Zinc alloys.

Summary of the Present Position.

Bibliography.

PART II.

CHAPTER V.

METHODS OF EXCITING EMISSION SPECTRA.

§ 72. There are four main ways of producing from a solid, liquid, or gaseous substance radiation suitable for its spectroscopic analysis : by means of the flame, the arc, the spark, and the vacuum tube. The vacuum tube will be dealt with in Chapter X. To these may be added the high-frequency spark and the exploded wire.

The wavelengths of the lines may change slightly as a result of changes in the length of arc, current, pressure, the effect of magnetic or electric fields, or the part of an arc from which the radiation is selected, but except in so far as they cause broadening of the lines, the changes are too small to be of any importance in spectrochemical analysis (Twyman and Smith, 1931). The same may be said of movement of the light-source in the line of sight, although the enormous velocities which occur in astronomical spectroscopy may cause the lines to be shifted far away from their normal positions.

In addition to the atomic lines due to the elements in the substance under examination, there are often present bands consisting of very numerous lines, often so close as to present in places an apparently continuous background. These form part of the molecular spectra mostly due to the products of combustion, which in the arc often consist of metallic oxides. It is claimed that the interrupted arc of W. Gerlach (§ 83) avoids this type of background. The glowing ends of the electrodes in an arc sometimes give a continuous spectrum strong enough to be noticeable. In the spark the lines of the oxygen and nitrogen of the air have a similar effect.

The air lines of the spark can be reduced in intensity by the use of an inductance (sometimes called a " Hemsalech coil ") in the oscillating circuit.

The effect of these "backgrounds" is discussed elsewhere (§ 67).

Flame Spectra.

§ 73. The Bunsen and Méker Flames.—Every chemist is familiar with the production of flame spectra. They are obtainable from certain metals or their salts when these are put into a Bunsen flame. The procedure in its simplest form is to make a small loop at the end of a piece of platinum wire ; to take up on the loop a small quantity of the substance (sometimes preferably moistened with hydrochloric acid)—or a drop of it if it be a liquid—and then to hold the loop, either by hand or by means of a convenient clamp, in the hot portion of the flame. With a Bunsen burner this will be the outer, and with a Méker burner the inner, portion. The substance is held in the lower part of the flame, to which a luminous glow is thus imparted, and on examination of this glow by means of a spectroscope the flame spectrum is seen.

Innumerable variants of the above device are to be found in the mass of literature which has accumulated since the time of Bunsen, who originated this method in 1859, but it suffices to state here that as far as analytical purposes are concerned :

(1) Flame spectra investigated in the above manner are of value only in identifying the alkali and alkaline-earth metals, with the addition of gallium, indium, and thallium.

(2) A spectroscope of low dispersion and high luminosity is best.

(3) The ultra-violet spectrum in flame spectra thus produced being too weak to have any value for analysis, a visual instrument is all that is required.

(4) Although in the case of sodium the phenomenon lasts a considerable time, yet in other cases, such as those of potassium and rubidium, it is very evanescent, and the observation should therefore be made at the instant of introducing the loop into the flame.

When attempting to detect the presence of extremely small quantities of potassium, rubidium, etc., the procedure of Gooch and Phinney (1892) may be adopted. They introduced their solution into the flame by means of a basket-shaped coil of platinum wire, which held about 0·02 ml. of liquid.

A very useful way of dealing with liquids has recently been published (Torok, 1939); it will automatically spray solutions of salts into a flame for a considerable time.

Under the flame of a horizontal Bunsen burner stands a porcelain crucible containing the salt solution, to which is added 1 : 3 hydrochloric acid and several chips of zinc. The evolution of hydrogen produces numerous small drops of fluid and carries them into the flame. The intense coloration of the flame lasts 5 to 10 minutes.

This method cannot be used with cations such as copper, tin, bismuth, and so forth, for which one adds to the acidified liquid a saturated solution of ammonium carbonate, thus evolving carbon dioxide. The gas evolution lasts about 10 or 15 seconds for each drop.

A third method uses a solution of aluminium chips in potassium lye, which greatly diminishes the intensity of the alkaline earths. As an example the various exposures are given with the non-volatile alkaline earths.

To make the visual observation of the lithium line more sensitive a solution of 0·14 per cent. coccinin, 0·0014 per cent. dahlia-violet, and 0·7 per cent. crystallized copper sulphate is interposed. With 0·3 per cent. lithium chloride in a sodium and potassium solution using a 2-cm. filter thickness, a carmine-red flame colour is clearly visible.

§ 74. The Oxy-Hydrogen, Oxy-Coalgas, and Acetylene-Air Flames.—The hotter the flame the more lines are emitted, so that with Lundegårdh's apparatus (acetylene-air) described *below*, 32 elements can be determined directly, namely

barium,
cadmium,
cæsium,
calcium,
chromium,
cobalt,
copper,
dysprosium,
gadolinium,
gallium,
gold,
indium,
iron,
lanthanum,
lithium,
magnesium,
manganese,
mercury,
neodymium,
nickel,
palladium,
potassium,
praseodymium,
rhodium,
rubidium,
ruthenium,
silver,
sodium,
strontium,
thallium,
yttrium,
zinc;

and the negative ions chloride, bromide, iodide, and sulphate by an indirect method. These hotter flames give also lines in the ultra-violet; for example, the lines used by Lundegårdh for indium include one at 2710·3 A., although most of the lines he used were of wavelengths greater than 3000 A.

H. Lundegårdh (1934) sprays the liquid into an acetylene-air flame from an atomizer, and finds this procedure is superior in constancy to either arc or spark ; he has used it with success in combination with a microphotometer in soil and plant analysis, and in physiological and pathological investigations. Although, in general, the spark and arc yield a more sensitive detection of many of the metals, Lundegårdh's method usually suffices in this respect for those which are of the greatest interest in such fields of work, and the accuracy attained (using a microphotometer) is very satisfactory. Lundegårdh says that the errors of determination never exceed 5 to 7 per cent., and with the alkalis, calcium, and manganese are not more than 1 to 2 per cent.* The method has been adopted by others with satisfactory results, and R. L. Mitchell (1936) claims an accuracy in determining the alkalis and alkaline earths of ± 4 per cent., which can be improved by repetition of the spectrograms. Determinations such as those of strontium in the presence of a large excess of calcium, which are scarcely feasible otherwise on a routine scale, present no difficulties.

Modifications of Lundegårdh's apparatus are described by Jansen, Heyes and Richter (1935), Heyes (1937), Lohse (1935), and Waibel (1935) ; Waibel in an earlier paper (1934) makes a comparison between the flame and spark methods. Bossuet (1935) uses the oxy-acetylene flame, into which he sprays the solution for the determination of cæsium in mineral waters.

Ramage, Sheldon and Sheldon (1933) used an oxy-hydrogen flame in the examination of biological material. They put the material to be analysed in a folded filter-paper, and placed this in an oxy-hydrogen flame. The method was simple, and although it did not approach the quantitative accuracy of Lundegårdh's, this is at least partly due to the fact that Ramage used no photometric means of measuring line intensities. It has been used in a survey of the micro-constituent elements of biological material (Webb and Fearon, 1937).

§ 75. A simple but very effective refinement was introduced by Steward and Harrison (1939) into Ramage's method, in determining the absorption of salts by various plant cells and tissues. They use an oxy-coalgas flame, carefully standardized by adjustment of the flow of the coal-gas and the pressure of the oxygen. The material is dried on filter-paper after the method of

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* Where accuracy is stated, the author means in every case the percentage of the amount of the constituent present.

Ramage (1929) and Ramage, Sheldon and Sheldon (1933). The papers, when dry, are rolled spirally into a tight spill, at each extremity of which is a region free from the dried sample. The improvement of the method consists mainly in the means taken to ensure that all the filter-papers are burnt in the same manner in the same part of the flame. This has been finally accomplished by the use of an apparatus consisting of three essential units: an asbestos screen, the burner with its ebonite mount and heavy stand, and the unit which carries the paper spill.

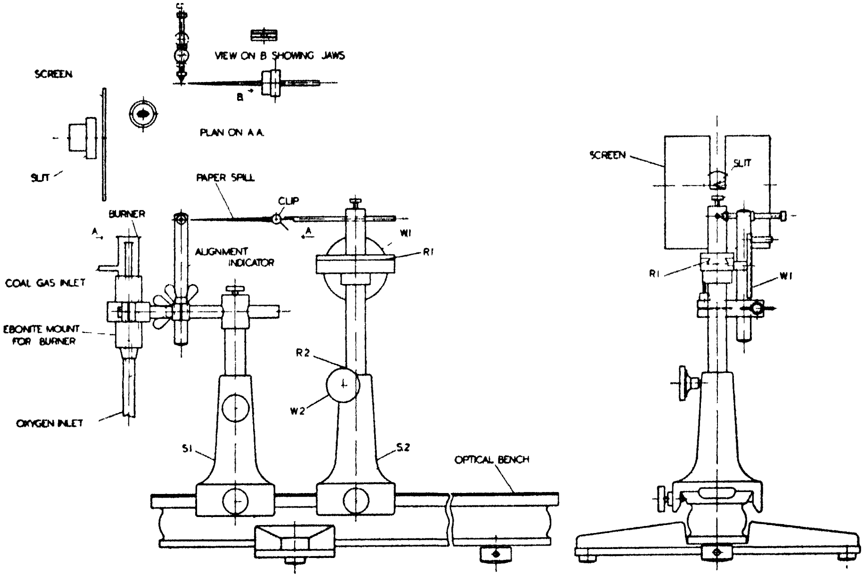

Fig. 23.—Vertical Section and End Elevation of Steward and Harrison's Apparatus.

The screen is placed between the flame and the spectrograph, so that only the light which passes through a wide slit reaches the spectrograph. The arrangement shown in Fig. 23 was satisfactory, and the spectrograms obtained were almost completely free from continuous spectrum.

Both the silica burner and the paper spill are carried on heavy rigid mounts attached to saddles S_1, S_2 on a rigid bar. This bar is in line with the spectrograph, and the technique depends upon the strict alignment of the paper spill, the flame, and the slit throughout the combustion.

The paper spill is held by a clip with jaws made to hold the flattened end (see plan on *AA* and view on *B*, Fig. 23). For any given position of S_2 the shaft and paper spill can be moved smoothly and horizontally along the axis of the bar for a distance somewhat greater than the length of the spill. The passage of the paper into the flame is controlled by the wheel W_1, which operates the rack and pinion R_1.

The flame has an outer and colder zone, within which is a sharply defined, hot, inner region at the edge of the oxygen cone. The saddle S_2 is moved along the bar rapidly from its first position until the tip of the spill reaches the hot zone of the flame ; then, by means of the wheel W_1, the approach of the spill can be so regulated that its brightly glowing tip, which is kept under observation through coloured glass, remains at the edge of the oxygen cone. In other words, the paper burns as quickly as it enters the flame, which should be neither so fast that it projects into the interior of the oxygen cone, nor so slow that combustion occurs in the outer and colder zone.

A microphotometer is used in evaluating the results, with an accuracy corresponding to a concentration difference of ± 2·5 per cent.

The Arc.

§ 76. In the arc all the metals, and in addition the five non-metals arsenic, boron, carbon, phosphorus, and silicon, reveal their presence by characteristic spectra. In the spark the scope is still wider, for many of the non-metals, among them fluorine, chlorine, bromine, iodine, oxygen, nitrogen, sulphur, selenium, and sometimes tellurium, become detectable as well as the metals, and the method is applicable to solutions as well as to solids, which is not easily the case with the arc.

Arc spectra may be classified as :

(i) Low-voltage (150- to 250-v. supply) D.C. and A.C. arcs.
(ii) Low-voltage (150- to 250-v. supply) D.C. arcs, interrupted.
(iii) Low-voltage carbon arc using the cathode layer.
(iv) High-voltage A.C. arc.

All these provide sensitive detection of small percentages, the most sensitive being (iii) and (iv).

§ 77. Low-voltage D.C. arcs require only simple apparatus, are cheap to run, do not consume much material, and are of wide general utility for qualitative and semi-quantitative work (*i.e.* for a quantitative accuracy of, say, ± 10 per cent.).

For metal or graphite electrodes D.C. electric supply of not less than 150 v. is needed as a rule, though Brownsdon and van Someren were able to deal with brasses on a D.C. supply of 120 v. If electrodes of about 5 or 6 mm. diameter are used the current is cut down by a simple resistance to from 2½ to 6 amp., according to the metal. The carbon arc will run on a D.C. supply as low as 80 v.

Higher currents are used for some purposes ; for example, for rapid sorting of alloy steels by visual inspection the pieces to be tested may be bars of substantial section, massive pieces (*e.g.* in the scrap-yard), swarf, or other forms of scrap for remelting. For such work currents of 7 to 12 amp. run a steadier arc and give a greater power of discriminating between various percentages of nickel, chromium, molybdenum, manganese, titanium, tungsten, cobalt, copper, tin, cadmium, and vanadium. In particular, the lines of nickel, which in the arc fluctuate in intensity, are steadier with the larger currents.

As a rough guide one may say that with rods of 5 mm. diameter 3½ amp. generally suffices, while for pieces of 20 mm. diameter 8 to 10 amp. may be required. Nottingham (1929) states that the relative intensities of the lines in the copper arc depend upon the current strength. Moreover, in the case of spark spectra the time of exposure varies with the shape and size of the electrodes. Thus it is necessary when quantitative work is being done that both current strength and size of electrodes should be standardized.

§ 78. Occasionally trouble may be encountered owing to oxidation of the specimen whilst the exposure is in progress. Hitchen (1933) had this trouble in his work on tin, but succeeded in overcoming it, the metal being kept in a reduced condition by the use of a small luminous coal-gas flame directed on to the surface of the molten tin.

§ 79. For many purposes electrodes of graphite or carbon, which are prepared specially for spectroscopic work, will be found useful ; pure graphite and carbon electrodes can now be bought, remarkably free from iron and other impurities.

Owing to the much greater thermal conductivity of graphites they do not form a white-hot positive crater as is the case with ordinary carbon poles, and in consequence the substance which is being analysed volatilizes more slowly. This is often a great advantage, especially in cases where minute quantities of powder are to be analysed. Small metallic or other specimens, powders, precipitates, dry residues from solutions, etc. can be placed in a hollow scooped out of or drilled into the lower graphite electrode to take the specimen. Graphite electrodes, however, will not run on A.C.

A useful variant of this procedure is to use copper electrodes, a few milligrams of the substance being placed on the lower electrode when the latter is hot. The substance adheres to the pole, and the spectrum of its metallic components is observable for some time. A pure copper electrode may also be used as the positive pole in examining a metallic object which it is desired not to disturb beyond a slight arc-burn. In either of these cases silver can be used instead of copper when the latter metal is being looked for.

Neuhaus (1938) describes a special form of arc, the object of which is to deal quickly with specimens which may be very small. In the factory of the International Nickel Company, in the spectrographic laboratory of which Neuhaus was working, the specimens might come in in the form of sheet, wire, tubing, or strip. It is part of the object of the design to prevent the specimens from getting too hot.

The specimen to be analysed is made the cathode ; this is normally the lower electrode. The anode or upper electrode consists of a sufficiently pure metal, preferably the main component present in the specimen, and has a cross-section of 0·25 in. × 0·25 in. Its lower end is cut to a slender cone with a point approximately 0·03 in. in diameter. The specimen is clamped in a copper holder with only 0·18 in. of the length of the former protruding from the holder. The copper clamp in turn is fastened by means of a set-screw to a copper radiator, arranged so that the long side of the cross-section of the specimen lies along the optical axis of the spectrograph. The radiator has twelve circular discs, which from the illustration in the paper one would judge to be about 3 in. in diameter. The arc gap is made 0·13 in., and the arc is operated at about 1·8 amp. on a 220-v. D.C. supply. A series resistance of 107·5 ohm and an inductance are connected in series with the arc.

§ 80. The sensitiveness of the arc can be enhanced, as pointed out by Milbourn (1934) in connection with the detection of minute amounts of impurities in copper, by using a globule of the sample (0·2 to 0·5 g.) as electrode in place of a solid rod (§§ 140, 176).

Piña de Rubies and Doetsch (1935) detected very minute percentages of certain metals by concentrating a constituent of a mineral placed in the arc by allowing the specimen to melt there and evaporate off the more volatile constituents.

§ 81. Metallic arcs will in general not run on A.C. supply, but where A.C. alone is available useful work may be done with carbon electrodes. For example, the late Sir Herbert Jackson used for many years (certainly before 1900) the following simple visual technique in qualitative analysis :

The image of an arc taking about 5 amp., and about 10 mm. long, is focussed by a lens on the slit of a wavelength spectrometer, and the position of the image is arranged so that the images of the white-hot carbons escape the slit.

The core of the positive carbon is removed with a small drill 2 mm. in diameter to a depth of about 6 mm., and the material under examination is introduced into the cavity. The arc is struck, and the spectrum examined for the particular line chosen. The advantage of placing the substance at the bottom of the cavity in the positive electrode is that the vapour of that substance, in whatever form it is given off, must necessarily participate in the emission of radiations from the arc.

For further particulars, and lists of suitable lines for visual spectrochemical analysis, Smith (1928) may be consulted.

The arc can be used with carbon, graphite, or copper electrodes to obtain the spectra of liquids. The poles may be heated by running the arc, and then drops of the solution may be allowed to fall on to the positive pole until it has cooled so that they no longer evaporate rapidly. The arc is then struck, and the exposure made.

§ 82. Effect of Polarity in an Arc whose Poles are of Differing Composition.—It used to be the practice when only one piece of a specimen was available for spectrographic analysis to use this as the positive electrode. Using the carbon arc it is the most usual procedure to place the specimen in the crater of the anode (*i.e.* positive electrode), which, when placed at the bottom, forms a convenient receptacle. This is also a satisfactory procedure when using graphite or copper electrodes.

On the other hand D. M. Smith (1933), investigating this question of polarity and using the arc between metals, concludes that when only one electrode is of the alloy under investigation, this electrode should be negative, as the impurity lines then approximate more closely to those obtained by having both electrodes of the alloy.

Brownsdon and van Someren have also observed that, in the case of brass containing aluminium, when the specimen is made the negative electrode and a specially purified brass rod the positive, the intensities of the aluminium lines are practically the same as if both electrodes were of the material of which the specimen is part. These workers in their examination of brasses use the specimens as negative electrodes only, and employ a rod of pure copper as the positive electrode.

When a technique of this type is employed it is necessary to observe certain precautions : the permanent electrode should be cleaned after use with each specimen : firstly, the rod should be filed with a rough file until the whole surface is bright ; secondly, the surface should be finished off with a file kept exclusively for that kind of metal of which the electrode is formed. Concerning the choice of polarity see also § 85.

§ 83. The Interrupted Arc.—With easily oxidizable or low-melting metals and alloys it is sometimes exceptionally difficult to obtain an arc which is steady in either position or character, and it was to remedy this that Gerlach and Gerlach (1934) introduced the interrupted arc. In the form used by Gerlach the electrodes are repeatedly brought into contact and separated, thus giving a transient arc ; the electrodes then do not get hot enough to be oxidized, and one thus avoids the almost continuous background, due to the complex molecular spectra, which causes difficulty in using the arc spectra of, for example, aluminium.

D.C. supply at 70 to 100 v. is used with a series resistance to limit the current when the electrodes are in contact to about 2 to 5 amp., according to their size and material. The resultant spectrum is not very luminous, but has few spark lines and bands. On principle it would seem that an arc having the advantages of relative coolness, comparative freedom from oxidation and fusing, and steadiness of position and character should be very useful. It has been applied by Gerlach not only to the readily oxidizable and easily fusible metals, but also to the platinum metals, partly in order to simplify the spectra, partly to avoid the selective volatilization of certain metallic impurities which he observed when these metals were arced in the ordinary way.

It is interesting to note that a similar device now in the Science Museum, London, was used by Wheatstone in 1833 in order to compare the spectra of " electric light " from the voltaic pile with that from an electromagnetic machine. Various common metals were used as electrodes, and Wheatstone described and charted their visible spectra, and recorded that each pattern of lines was characteristic of the metal itself, thus laying the foundation for metallurgical spectrochemical analysis (Wheatstone, 1835).

This method has not been at all widely adopted ; possibly the form described by Pfeilsticker (see *below*) may become more popular.

§ 84. **Interrupted Arc operated by High-frequency Current.**—Pfeilsticker (1937) describes a way of avoiding the necessity of moving the electrodes to interrupt the arc. The electrical circuit is shown in Fig. 24. C_1FT is a high-frequency circuit, fed from the transformer *Tr* (*J*), which takes a current of about 0·5 amp. at 220 v. A.C. C_1 is a capacity of 0·0043 μf.

Two zinc plates of 4 cm. diameter form the spark gap *F*. These plates have circular grooves, and are from 2 to 3 mm. apart. The condenser C_1 discharges across this spark gap through the primary coil of the high-frequency transformer *T*, which has 16 turns of 2-mm. diameter bare copper wire, the windings being 35 cm. in diameter and spaced 2 cm. apart.

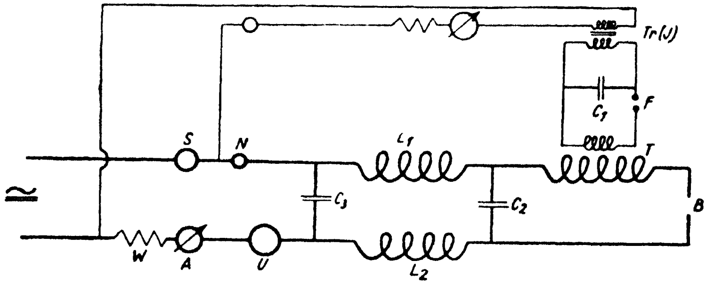

Fig. 24.—Electrical Circuit for an Interrupted Arc operated by means of a High-frequency Current.

The secondary coil has 140 turns of 1-mm. covered copper wire of 26 cm. diameter, but the author considers that somewhat thicker wire with fewer windings would be preferable. The high-frequency current induced in the secondary coil sparks across the gap *B* between the electrodes which are to be analysed, and passes through the condenser C_2 (capacity 0·00044 μf.) back to the coil. The secondary coil and *B* are traversed also by the low-voltage current, which comes from the supply through the self-induction coils L_1 and L_2, the interrupter *U*, a resistance *W* (220 ohm, 10 amp.), and an ammeter *A* (up to 10 amp.). The self-inductances L_1 and L_2 are to prevent the high-frequency current from getting back to the supply conductors, where it might cause short-circuiting or other trouble. L_1 and L_2 must have large inductance, but should have as small a capacity as possible. The author uses 2 coils each of 50 turns of 10 to 12 cm. diameter, 1 cm. apart. In the middle of each coil is an iron core.

This arrangement does not entirely bar the high-frequency current, but the introduction of the condenser C_3 (capacity 0·0018 μf.) makes this harmless. The switch S turns off the low-voltage and high-frequency circuits simultaneously, while the switch N controls the arc current only.

The interrupter itself can be very simple. A disc of insulating material (Fig. 25) fits direct on the spindle of a $\frac{1}{25}$-H.P. motor, bearing copper conductors against which press three spring contacts. All three of the conducting plates on the disc are connected together. In position (3) of the control switch the arc current is allowed to pass for one-quarter of the time, in position (2) for one-half of the time, while in position (1) the interrupter is short-circuited so that the arc is not interrupted at all. A condenser C_4 is put in parallel (capacity 20 to 40 μf.). If A.C. is used this condenser (which with A.C. is not necessary) must be omitted, otherwise the arc will not be interrupted, since the A.C. is transmitted through this big capacity. The motor has separate winding for field and armature, the armature being fed with current at controlled voltage so as to be able to vary the speed without loss of power. In using A.C. a speed reduction must be employed.

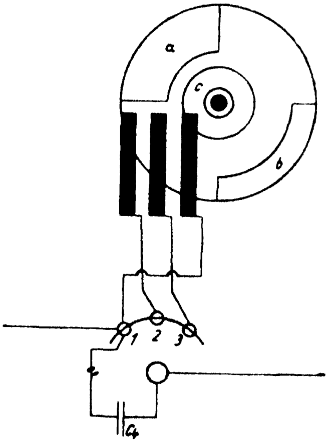

Fig. 25.—Interrupter.

The radiation of the electrodes is determined solely by the low-voltage arc, that of the high-frequency current being negligible. The high-frequency current serves only to strike the arc. This arc gives much more radiation than the mechanically operated one.

A principal advantage of this form of the interrupted arc is that, although the electrodes are fixed, yet the spark, wandering over the end surfaces of the electrodes, carries the arc with it, so that it plays all over those surfaces. Further, the ordinary arc stand can be used. The author mentions as being used with his arc substances so diverse as aluminium and blood or serum. Dry organic material, liver, for example, can be examined, using auxiliary electrodes, without the striking of the arc being prevented or the specimen falling off.

§ 85. Mannkopff and Peters' Carbon-arc Cathode Layer (Glimmschicht) (Strock, 1936).—A very high degree of sensitiveness is obtained by the carbon-arc cathode-layer method developed by Mannkopff and Peters under Professor V. M. Goldschmidt at the University of Göttingen. A full description of the method is given in the reference, together with an account of an improvement by Strock.

The work in Goldschmidt's laboratory was concerned with the detection of very small quantities of the elements in powdered rocks, minerals, and soils, the experiments being carried out for the purpose of deducing the fundamental laws which govern the distribution of the chemical elements in Nature.

The spark method was out of the question, because most of the samples to be analysed were non-conducting, and it was desirable to analyse the samples directly, without chemical treatment, to avoid the introduction of any impurities from chemicals, crucibles, ashes, etc. The carbon arc was selected, the portion of the spectrum observed being in the immediate vicinity of a hole in the cathode, in which the specimen was placed.

By this method smaller quantities of most elements in powdered rocks, minerals, soils, etc. can be determined than with the spark or previous arc methods. No previous treatment (except powdering) is required, and only a few milligrams of material is necessary. Most metals can be determined in concentrations down to 0·0005 per cent., while 10 to 20 times this sensitivity has been observed. It has also been found that the intensity ratio of two lines in the cathode layer is more constant than in the arc gas column.

In contrast to earlier carbon-arc methods, which vaporize the substance from the anode (positive electrode) (§ 82), this method vaporizes the sample from the cathode. Mannkopff and Peters found that the line spectra of most elements are from 10 to 100 times stronger immediately in front of the cathode than in the arc gas column. The recommendation of many workers to-day to use the middle portion of the arc column in analytical work therefore results in a failure to utilize the full effective sensitiveness of the carbon arc, especially when small quantities of material are employed for the analysis.

The spectrum of Fig. 26 illustrates clearly the cathode-layer effect upon which Mannkopff and Peters based their new and

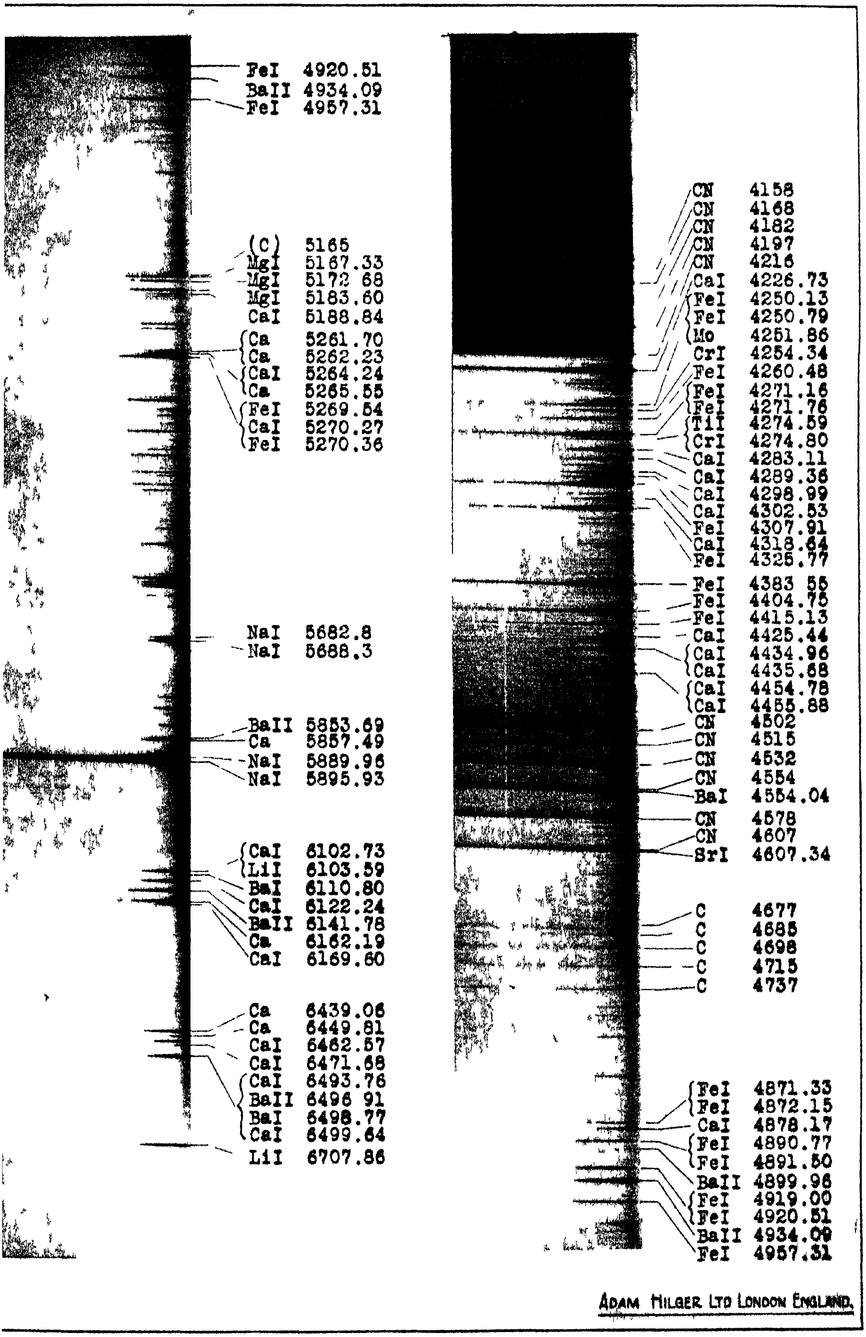

Fig. 26.—Cathode-layer Effect.

widely applicable method of quantitative spectral analysis. This is the spectrum of an impure carbon rod, produced with an 8-amp. D.C. current with a 5-sec. exposure on a large quartz spectrograph. The burning arc was focussed sharply on the spectrograph slit for making this photograph, so that the vertical distribution of the light in the arc column is revealed by the vertical variation in blackening of the spectrum itself. The black streak at the bottom is the continuous light from the cathode, which was constantly regulated to keep its image fixed just on the upper end of the spectrograph slit. The varied length and shape of the lines are very obvious. Most of them are more intense towards the cathode, decreasing in intensity in the direction of the anode.

Mannkopff and Peters found, for example, that for small amounts of zinc, copper, and cadmium the lines in the cathode layer were 5 to 10 times more intense than in the main arc gas column. The effect is still stronger for the elements of the first three groups of the Periodic System and for silicon, tin, lead, bismuth, iron, nickel, cobalt, scandium, etc., in which the intensity of the lines in the cathode layer is frequently 100 times stronger than in the gas column. At times certain lines are very intense near the cathode, but vanish completely in the arc column. By employing a larger quantity of substance for the analyses, the cathode-layer effect is reduced or even disappears. The sensitivity of this method is therefore usually greater when smaller quantities (1 to 3 mg.) are employed. The use of a larger amount of sample in the arc rarely, if ever, leads to increased sensitivity, as, not only does the continuous light then mask the lines, but also the danger of contamination of the carbons is increased, and the sensitive cathode layer is destroyed. With this method, therefore, two of the chief requirements of a spectral analytical procedure are realized, in that a high sensitiveness is attained and only a very small amount of sample is required.

Naturally, with such a high sensitivity the disturbing influence of impurities and contamination of the materials used must be constantly borne in mind. This requires above all that carbon electrodes of almost absolute purity should be used. Such carbons were first produced in Göttingen, and placed on the market especially for this purpose, but are now obtainable from other sources also. The second requirement of this method is a spectrograph of sufficiently high dispersion to separate the rather large number of lines which appear in the arc spectra of a more or less complex mixture. This high dispersion is also necessary in order to separate the line spectra from the numerous lines of the CN and C_2 bands which appear strongly in the carbon arc when only a little substance is being vaporized and the arc-gas temperature is high. In the cathode-layer method the short wedge-shaped lines of the line spectra can be readily distinguished from these longer band lines. The intensity of the carbon arc is so high that a spectrograph of small aperture can be used. In fact it is frequently necessary to weaken the light beam to be analysed in order to avoid over-exposure of the photographic emulsion.

§ 86. The High-voltage A.C. Arc. At least as great sensitiveness as the above seems to be attained by the high-voltage A.C. arc used by Duffendack and Wolfe (1938) and by Owens (1938*b*). The advantages claimed include ease of maintenance, high sensitivity, low background density, and accuracy. A comparison made by Owens of the spectral sensitivities of detection of impurities present as traces in different sources of emission gave the following results :

The sensitivities of detection in the A.C.-arc and cathode-layer sources of iron, silicon, manganese, calcium, aluminium, strontium, and copper in sodium hydroxide are comparable, that in the D.C. arc is somewhat less. The sensitivity of detection of vanadium in sodium hydroxide is comparable in the A.C. arc and the cathode layer, but is fivefold lower in the D.C. arc. The sensitivity of detection of phosphorus in acid sodium phosphate solutions and of silver in sodium chloride solutions is from five- to tenfold greater in the A.C. arc than in the cathode layer and the D.C. arc. In general, the sensitivity of detection in the A.C. arc of any metallic constituent of a chemical material is of the order of magnitude of 0·0001 per cent.

Summing up, it is concluded that for the analysis of many industrial chemicals the sensitivity of the high-voltage A.C. arc is comparable with, or greater than, that of the cathode layer, while that of either is, in general, greater than that of the whole D.C. arc. However, neither the high-voltage A.C. arc nor the cathode layer shows, in general, a greater sensitivity for the analysis of solid alloys than does the D.C. arc. The advantages of the A.C. arc over the cathode layer for quantitative analysis consist in much weaker background radiation, uniformity of line intensity throughout the entire usual arc length, and elimination of any optical system for accurately focussing a restricted portion of the arc upon the spectrograph slit.

The author does not give particulars of how the solutions were applied, but in all probability it was as described by Duffendack and Wolfe (1938), in which a glass rod is dipped into the solution and the ends of the electrodes are touched with the droplet on the end of the rod. The solution is dried, leaving the ends of the carbons covered with a thin film of solid material.

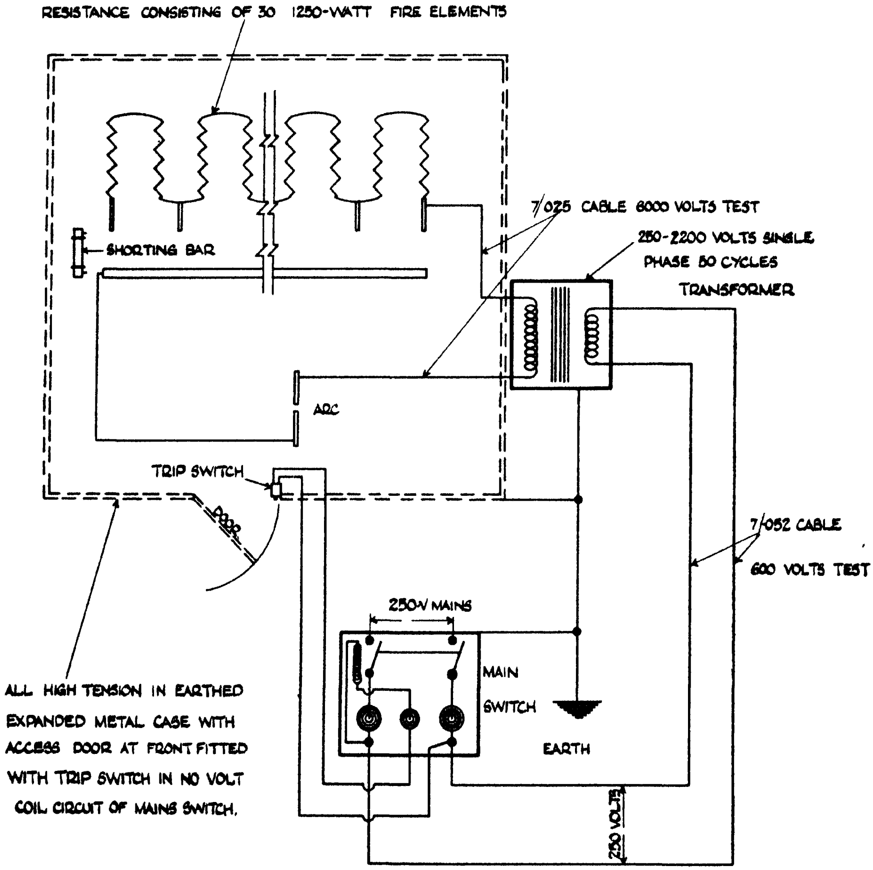
RESISTANCE CONSISTING OF 30 1250-WATT FIRE ELEMENTS
SHORTING BAR
7/025 CABLE 6000 VOLTS TEST
250-2200 VOLTS SINGLE PHASE 50 CYCLES TRANSFORMER
ARC
TRIP SWITCH
7/052 CABLE 600 VOLTS TEST
250V MAINS
MAIN SWITCH
EARTH
250 VOLTS
ALL HIGH TENSION IN EARTHED EXPANDED METAL CASE WITH ACCESS DOOR AT FRONT FITTED WITH TRIP SWITCH IN NO VOLT COIL CIRCUIT OF MAINS SWITCH.

Fig. 26A.—Circuit Diagram for High-voltage A.C. Arc.

The reader interested in this kind of work should refer to all the papers mentioned *below*.

The A.C. arc in question is obtained from transformers permitting voltages of 1100, 2200, or 4400 to be obtained. Two transformers are used, either of which may be used as a variable secondary impedance in series with the arc gap to control the arc current, or may be entirely removed from the circuit. A variable iron-core inductance in the primary circuit controls the maintenance of the arc.

The high-voltage A.C. arc is also used by I.C.I. (General Chemicals), Ltd., Central Laboratory, Widnes, England, to whom I am indebted for the following description. The circuit is shown in Fig. 26A.

The resistance in the secondary circuit is built up by connecting thirty 1250-watt electric fire elements in series, a tapping point being provided at the end of every pair. The best value of the resistance for the particular work in hand may be readily found by experiment. These resistances must be of such dimensions that they are not strongly heated during prolonged operation of the arc, otherwise constancy of excitation conditions cannot be maintained.

As the arc is operated in a secondary circuit of considerable power (approximately 7 H.P.), adequate insulation and protection against shock must be provided. The high-voltage A.C. arc is self-starting, but operates only on short arc gaps (0·5 to 1·5 mm.), and a special arc stand capable of such fine adjustment was built to suit these conditions.

For further particulars of the high-voltage A.C. arc and its uses the reader should consult Duffendack and Thomson (1936), Owens (1938*b*), Duffendack and Wolfe (1938), Duffendack, Thomson, Lee and Koppius (1938), Owens (1939), and Hess, Owens and Reinhardt (1939).

§ 86. 1. Rollwagen (1939) records a number of physical factors determining the phenomena occurring in the arc discharge. The fundamental difference between the conditions in the positive column and those in the cathode layer is discussed. In the positive column the electrons are approximately in thermal equilibrium with the gas atoms, and this equilibrium therefore determines the radiation. In the cathode layer, *i.e.* the ion layer separated from the cathode by a distance equal to the free path of the electrons, the electron temperature is much higher than the gas temperature, and therefore much higher atomic energy levels are produced.

The effect caused by the arc on the anode can be described as thermal vaporization, whilst on the cathode the effect is more similar to a mechanical spraying. The author quotes Breckpot as finding that the Pb : Cu intensity ratio decreases owing to partial volatilization of lead if the material is used as anode, whilst the intensity ratio is constant when the material is used as cathode.

The arc temperature depends on the ionization potential of the main constituent of the vapour in which the arc is running. By altering the concentration of an element present in the arc vapour, the arc temperature, and consequently the intensity ratio of the lines of other elements present, can be affected. By running the arc mainly in potassium or sodium vapour, with an ionization potential considerably lower than that of the element in question, this effect may be eliminated. For this purpose he uses carbon electrodes impregnated with a sodium salt.

The influence of electrode shape, gap width, electrode-surface qualities, and other factors is discussed in a general, qualitative manner.

The Spark.

§ 87. The Condensed Spark.—The condensed spark referred to by Hartley, Pollok and Leonard, and de Gramont is obtained by the arrangement shown in Fig. 27. The high-tension current from an induction coil or (in recent years, on account of the difficulties with contact-breakers and the maintenance of constant operating conditions) a small high-tension A.C. transformer is applied across the leads at *E*.

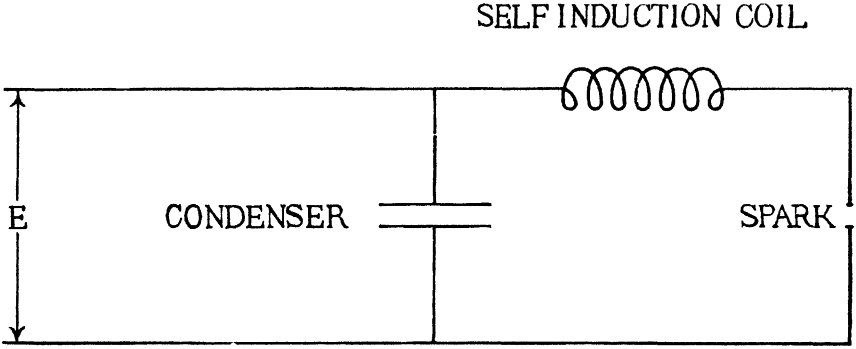

Fig. 27.—" Standard " Electrical Circuit, for Condensed Spark.

The currents in such a circuit are as follows :

The voltage *E* of the transformer rises and falls with the same periodicity as that of the generator from which the transformer is fed—say 50 to 80 periods per second. On its rise it charges the condenser up to such a voltage that the dielectric (air) in the spark gap breaks down, and the condenser then discharges through the spark gap. As soon as the spark passes, the air becomes ionized, and the resistance drops to a value which depends on the number of ions available for carrying the current.

Owing to the inertia effect of the self-induction an oscillatory discharge is produced, with the result of a series of sparks in rapid succession. Even when no self-induction is deliberately introduced, there is sufficient in the connecting wires to produce the oscillations, which are then very rapid, and it is with this arrangement that the spectrum of the discharge has its most distinctively "spark" character.

Following the well-known formula

$$n = \frac{1}{2\pi\sqrt{LC}},$$

where n is the number of oscillations per second, L the self-induction in henries, and C the capacity in farads: with a capacity of 0·006 microfarad the number of oscillations per second would vary from $8{\cdot}4 \times 10^5$ to $6{\cdot}5 \times 10^4$ when the self-induction varies from 6 microhenries to 1 millihenry, the oscillations being slower with the larger self-induction.

The phenomenon does not follow so strict a law as this, for not only is resistance present in the oscillating circuit, but this resistance is variable—see *below*.

Owing to the presence of resistance the oscillating current dies away, ceasing altogether long before the voltage E acquires a value high enough to start another train of sparks. As the oscillating current dies away there is also a corresponding diminution in the rate of ion formation, and as a consequence an increasing effective resistance of the spark gap.

On increasing the capacity C the oscillations will become slower, but since the quantity of electricity stored in the condenser before it is discharged is greater, there is a correspondingly greater quantity of electricity to pass at each oscillation. The average current during the train of sparks (and also the amount of energy expended in the spark gap) would be the same as with less capacity, but for the fact that with increased capacity there is a less rapid decrement of the discharge at successive oscillations, with a commensurately slower decrease in the ionization. Thus there will be a more prolonged train of sparks and an emission of radiation for a longer time, with a higher temperature of the electrodes consequent on the greater effective duration of the oscillating current.

The increased capacity results in the circuit taking a greater quantity of the current from the transformer and generator. With gradually increasing capacity this process continues until the maximum output of the transformer and the generator is insufficient to charge the condenser to the potential requisite to break down the spark gap, when it becomes necessary to approach the electrodes closer together, or to use a transformer of greater power.

It will be seen from the formula that the oscillations are also made slower if, instead of the capacity being increased, additional self-induction L be introduced into the circuit.

The oscillatory nature of the spark can be demonstrated by directing a beam of rays on to a photographic plate by way of a mirror which is rapidly rotating, or by photographing on to a moving plate or film. Figs. 27A and 27B show such photographs obtained by means of a rotating mirror, and reproduced from a paper by Kaiser (1938).* In Fig. 27A, where the capacity and inductance are relatively small, the oscillations are very rapid, and are barely resolved. In Fig. 27B, where capacity and inductance are larger, the oscillations are much slower, and the separate discharges can be distinctly seen.

Thus we have an explanation of the changing character of the spark. With small self-induction the following phenomena predominate :

(*a*) A comparatively cold spark gap. Presence of air lines in the spectrum, due to ionization of the air, there being only very little of the metallic vapour present.

(*b*) A steep potential gradient in the spark gap, causing high velocity of the ions, sufficient to excite the higher stages of ionization.

(*c*) The metallic vapours which are present are not due in any great part to volatilization through the electrodes becoming hot.

With increase in self-induction the quantity of metallic vapours present becomes greater, as the temperature of the electrodes rises. The lower resistance of the spark gap lowers the average electron speed, so that the excitation is of a lower degree, thus bringing out the characteristic arc or fundamental lines.

The self-induction coil (used by Pollok and Leonard, and de Gramont, but not by Hartley) is often referred to as a ***Hemsalech coil.*** Its chief use is to reduce the intensity of the lines due to air.

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* These photographs were taken with the Feussner spark generator referred to in § 87. 1.

This form of outfit was first brought to my notice in 1913 by Dr. P. G. Nutting. Most workers in Europe find their purposes well served by a ¼-kva. set, the transformer having a voltage of 15,000 when running on open circuit without condenser. It is so widely used that we may refer to it as the " standard " sparking

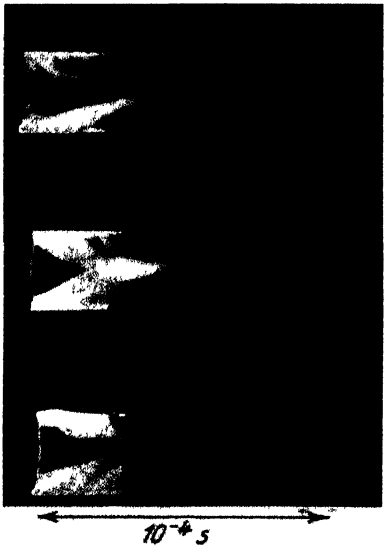


Fig. 27A.—Photograph of Lead Spark obtained by means of a Rotating Mirror (L 0·08 mh., C 0·001 μf.).

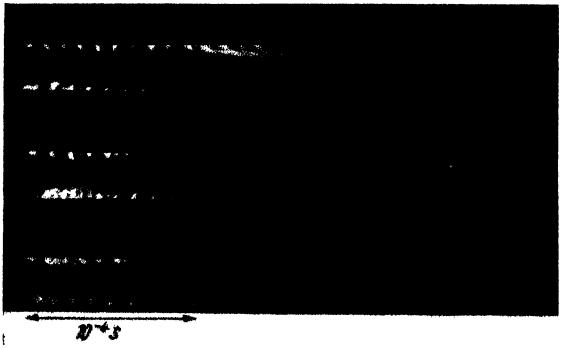
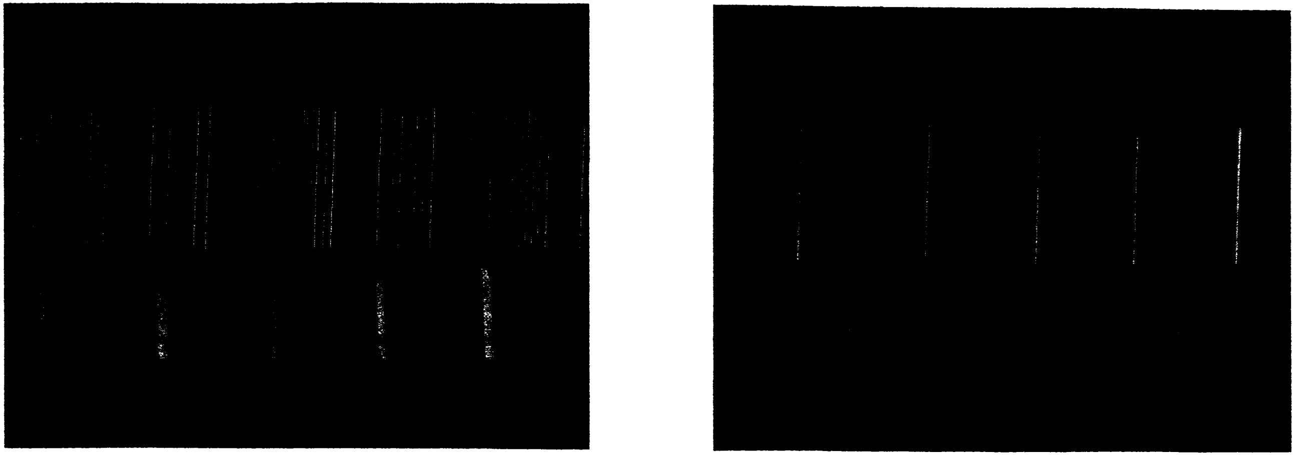


Fig. 27B.—Photograph of Aluminium Spark obtained by means of a Rotating Mirror (L 0·8 mh., C 0·003 μf.).



(1)	
Spark gap	3 mm.
Capacity, *C*	0·0015 μf.
Self-induction, *L*	Nil.
Voltage of transformer output	13 kv.

(2)	
Spark gap	3 mm.
Capacity, *C*	0·005 μf.
Self-induction, *L*	0·25 mh.
Voltage of transformer output	13 kv.
Auxiliary spark gap (Cu)	5 mm.

Fig. 27c.—Photographs of Zinc Spark obtained by means of a Falling Plate.

circuit ; it produces what is often called a "simple oscillating," sometimes a "simple condensed," and sometimes a "simple resonant," spark.

Much more powerful sets are in use in the United States ; Owens, for example (1938), uses sets of 1 kva., 25,000 v., and 10 kva., 50,000 v. One would expect these more powerful sets to bring a larger volume of material into radiation, and thus possibly to reduce irregularities due to microscopic heterogeneity, but I have not seen this adduced in their favour by those who use them.

Details are given in Chapter IX of the capacities and inductances suitable for various analyses.

§ 87. 1. It was pointed out by Twyman and Smith (1931, p. 20) that the usual circuit may give, with such a distance between the electrodes as is employed in spectrochemical work, a number of separate flashes for each period of the primary frequency, each flash consisting of a train of oscillating discharges as already described. These separate flashes are due to the voltage being built up, discharged, and built up again a number of times during each cycle of the A.C. supply.

It has been found in the author's laboratory, for example, that with a capacity of 0·0015 μf. there is a whole series of separate flashes during each half-cycle, of varying intensities. This is illustrated in Fig. 27c (1), obtained by means of a falling photographic plate ; the broad lines indicate time-intervals of $\frac{1}{100}$ second, *i.e.* one half-cycle of the A.C. input. The illumination of the slit was of type (*ii*) (§ 54).

The circuit found in the author's laboratory to be best suited to spectrochemical analysis of zinc-base alloys has a capacity of 0·005 μf. and an inductance of 0·25 mh., and includes a subsidiary spark gap in series with the gap under examination (§§ 89, 230). With this circuit the successive sparks—Fig. 27c (2)—are much more uniform in time and intensity, and one would expect, as is found, a greater uniformity in the excitation of individual spectral lines.

Some workers, observing the type of spark shown in Fig. 27c (1), and attributing to the irregularity of the discharge the lack of consistency between repeated analyses of the same specimen, have designed apparatus to isolate the first of each series of flashes.

Sawyer (in the United States) tried an oscillating circuit employing valves, but abandoned it in favour of the circuit mentioned *below*.

Four other systems have been put forward with this purpose :

(*a*) *Sawyer and Becker* (1923).—This was the earliest system of the kind now in question, and used an arrangement in which the condenser was charged with D.C. and switched over by hand about every three seconds. Kosbahn (1936) has investigated this circuit, with and without damping. He finds sufficient damping for his purpose if no self-induction is used, and says that the spectrum is then " absolutely reproducible."

(*b*) *Feussner Spark* (*Zeiss* " *Funkenerzeuger* ").—In the Feussner spark (Fig. 27D—Kaiser, 1938) : (i) only the first of each train of sparks is allowed to occur ; and (ii) only the first few high-frequency oscillations of this spark are permitted.

Condition (i) is achieved by a rotary interrupter driven by a synchronous motor, which completes the circuit by means of a subsidiary spark gap for only a short time every half-cycle of the A.C. mains.

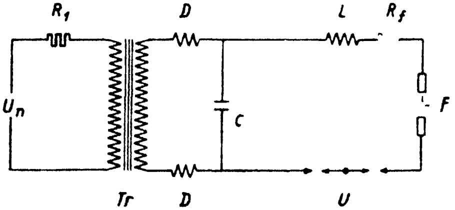


Fig. 27D —Feussner Spark Circuit.

(An alternative means of doing this is to tune the transformer secondary circuit to resonance with the mains frequency ; but this makes a complicated arrangement and is not recommended.)

Condition (ii) is achieved by additional damping in the circuit to absorb the energy of the oscillations, in the form of a quenched spark or a second circuit tuned to resonance with the spark circuit and inductively coupled to it.

It is claimed that since with the subsidiary spark of the rotary interrupter the total spark length is increased, inadvertent variations of the main spark gap are of less importance in affecting the discharge conditions.

A further feature is the blowing of air on to the spark gap to remove the ionized vapour, which otherwise might be expected to make successive sparks take place under different conditions and could cause reversal of the lines. It is further claimed that irradiating the spark gap by a mercury lamp de-ionizes the gap, and is advantageous.

(*c*) *The Post Office Research Laboratory*, Dollis Hill (unpublished report), in 1935 independently developed a circuit of the type in question. This uses rotating contacts driven by a synchronous motor at 3000 r.p.m. to charge the condenser and then discharge it after the charging circuit has been broken. This gives one flash per cycle, as in the Feussner spark.

(*d*) *Vincent and Sawyer* (1937) used a simpler form, including a synchronous interrupter, but with a series resistance instead of a quenched spark or tuned circuit.

The claims first made for the Feussner circuit were not substantiated by figures, but in 1936 Kaiser, working in the Zeiss physical laboratory, and taking great care to keep the conditions of working constant, found that with one alloy (antimony in lead—about 0·5 per cent.), neglecting 5 per cent. of his readings, all the remaining readings were within 2·64 per cent. of the mean.

Kaiser's paper is an important one on account of the large number of readings taken on one specimen, the careful treatment of the readings to get the best possible average, using the customary Gauss routine, and the complete way in which the conditions are stated.

The present writer has, however, seen no evidence that the same degree of accuracy is not attainable by the use of the ordinary sparking circuit. Working with liquids and using the latter circuit, Duffendack had in 1933 claimed an accuracy of 1 per cent., and the present writer, who had the privilege of seeing Duffendack's notebooks in 1933, was satisfied that this statement was substantially correct. This confirms that the chief cause of occasional discrepancies between chemical and spectrochemical analyses is the heterogeneity of the specimen.

Further, measurements were made in my laboratory, using the " standard " sparking system, on an alloy of the same composition as that which Kaiser used. The result was equally as good as Kaiser's.

Kaiser himself found that with determinations other than those of antimony in lead he did not get the same accuracy. The reason is not far to seek. The limit of solid solubility of antimony in lead at the eutectic temperature (247° C.) is 2·94 per cent., so that at this temperature the antimony in the above alloys would all be in solution. The solid solubility appears to decrease with fall in temperature, and at room temperature is probably extremely low. However, one would not expect there to be any free antimony in an alloy containing 0·5 per cent., and actually in a micro-specimen containing 0·62 per cent. of antimony it was not possible to detect any free metal. Thus as the antimony is probably in solid solution, one would expect it to be distributed in a uniform manner throughout the specimens, and to get consistent results with it.

§ 87. 2. Spark with Controlled Intensity.—Badum and Leilich (1937) used in conjunction with the Feussner spark an intermediate image (*Zwischenabbildung*), which was used to control the spark intensity by means of a selenium barrier-layer photocell connected to a galvanometer. The authors claim that if during the exposures the deflection is kept constant by regulating the spark-gap width, the consistency of analyses is very much improved.

§ 88. Capacity and Self-induction.—The amounts of capacity and self-induction used by various investigators differ considerably, and a number of papers have been published describing the effects of the systematic variation of these quantities.

Meggers, Kiess and Stimson (1922) state that it is desirable to have various quantities of self-induction for insertion in the secondary circuit, a serviceable range in practical spectroscopy being from about 0·00007 to 0·005 henry. Also the capacity should be of the order of 0·005 μf. or more. The following formula is given for the calculation of single-layer inductances (in henries), which can be constructed by winding coils of insulated wire on wooden or pasteboard cylinders :

$$L = 4\pi n^2 lA \times 10^{-9},$$

where A is the area of cross-section of the solenoid in sq. cm., l the length in cm., and n the number of turns per unit length.

In my laboratory it has been found that for the detection of the smallest traces of metallic constituents very small self-induction is in general desirable ; particulars on this point are given in Chapter IX in dealing with various metals and alloys.

§ 88. 1. High-frequency Spark.—The application of a high-frequency Tesla discharge to the determination of traces of mercury in filter precipitates, electrolytic deposits on thin foils, and biological sections is described by Gerlach and Schweitzer (1931*a*) and Gerlach and Gerlach (1934). The high-frequency current in an oscillating spark circuit induces a vigorous high-frequency discharge in a further circuit containing the spark gap for analysis.

Metallic spectra obtained with this arrangement are arc-like in character, the spark lines being suppressed, and it is claimed that the better vaporization of the material for the discharge renders the high-frequency method more efficient for analytical purposes than that of the ordinary condensed spark. It does not appear that any industrial laboratories use this method except to test a given spot in the metal—this type of spark can be located very precisely. For the analysis of filter residues the lower electrode of the spark consists of a dielectric plate (of 1- to 2-mm. thick glass or quartz) supported on a metal plate, the filter being placed on the dielectric plate at a short distance from the upper electrode.

§ 88. 2. In Table V the different ranges of capacity and self-inductance employed by various investigators are collected together, and for purposes of comparison the values are all given in microfarads and millihenries.*

TABLE V.—RANGES OF CAPACITY AND SELF-INDUCTANCE EMPLOYED BY VARIOUS INVESTIGATORS.

Investigator.	Year.	Capacity, microfarad.	Self-induction, millihenries.
Hemsalech . . .	1899	3 Leyden jars	0·12–3·8
A. de Gramont . .	1902, 1921	0·008–0·2	0·08–22
Bureau of Standards .	1922	0·005	0·07–5
Bassett and Davis .	1922	0·06	0·2
Hull and Steele . .	1927	0·02 (effective)	0·059
Gerlach and Schweitzer	1927, 1928	0–0·013	0·5
Scheibe and Neuhäusser	1928	0·0017–0·0067	0·002–0·056
Hilger laboratory .	1939	0·005	0·03–1·0
Ryde (explosion method)	1926	0·01–0·05	0·2

§ 89. Tandem Spark (Zehden, 1940).—The introduction of an auxiliary spark gap in series with the analysis spark has three effects improving spectrochemical analysis in certain cases :

The first effect to be mentioned is a general increase in intensity. This allows one either to use lines which are too weak with the single spark, or to cut down the exposure-time. When analysing, for instance, copper-cadmium alloys, the lines Cu 2303 and

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* Centimetre units are sometimes used for both capacity and self-induction. To convert such data into the more generally used units of microfarad and millihenry : the capacity in centimetres divided by 900,000 will give the value in microfarads ; and 1 millihenry is equal to 1,000,000 cm. of self-induction.

Cd 2313 give intensities suitable for microphotometric measurements with the tandem spark and 40 sec. exposure, whilst with the single spark, all other conditions being the same, they are hardly visible on the spectrogram. When using the lines Cu 2276 and Cd 2265, the exposure-time may be cut down from 40 sec. with the single spark to 15 sec. with the tandem spark. When analysing the main constituents of " Mazak " zinc-base alloys, by introducing the tandem spark the exposure may be cut down from 45 sec. to 30 sec.

But not only is the absolute intensity increased ; there is also an intensity increase of certain lines relative to other lines and to the background, resulting in the tandem-spark spectrum containing more lines than the single-spark spectrum. When analysing, for instance, " Electron " magnesium-base alloys or " Mazak " zinc-base alloys containing traces of iron, under the same conditions as those which give suitable densities for the main-constituent lines, the iron lines 2382 and 2396 A. are visible quite distinctly from the background when using the tandem spark, whilst in the single-spark spectrum they do not appear.

Finally, the tandem spark is very useful for stabilizing the spark and the sparking conditions, particularly for samples with bad surfaces (sharp edges, irregular oxide film, and so on). When sparking, for instance, " Mazak " zinc-base samples one can see from the deflections of the ammeter in the primary transformer circuit that the current fluctuations with the tandem spark are considerably smaller than with the single spark, and the consistency of the results is better. From small metal pieces with more or less sharp edges (*e.g.* turnings) it is almost impossible to obtain a good spark in the usual way, since such electrodes grow red-hot at once, and the spark becomes very weak. But with a well shaped auxiliary spark gap in series, even from knife-edges a powerful spark is obtained without overheating the electrodes. The tandem spark has also proved useful for sparking liquids, both with regard to the consistency and to the intensity obtained.

As auxiliary spark gap a 5-mm. gap is used formed by 5-mm. diameter copper rods with flat polished ends. The sparking surfaces keep smooth for a long time in spite of the oxide film. The analysis spark gap is 3 mm.

§ 90. Solids, including Powders.—The specimens for sparking are held in an adjustable arc and spark stand (§ 53). This suffices for metals, alloys, or conducting minerals. A technique for obtaining the spark spectra of non-conducting powders, such as those of slags, stony minerals, glasses, and precipitates and residues from solutions, has been developed by de Gramont (1921*a*). The lower electrode is a stout platinum wire supporting a small cup of platinum about 20 mm. in diameter and 5 mm. deep, in which the substance under examination is mixed and fused with about four times its weight of very pure sodium or lithium carbonate, the fusion being kept liquid by heating the cup with the flame of a Méker burner. The upper electrode is a second platinum wire.

§ **91. Liquids.**—If the samples are in the form of solutions, a sparking tube may be employed. The first tube of the kind was used by Hartley (1884), who used graphite electrodes because of their simple spectrum. This method was subsequently improved by Pollok, who used gold electrodes (see also § 111). Improvements since then have been directed towards avoiding the spectrum of the electrodes, minimizing the sputtering of the liquid, and preventing the formation of scum on the surface of the liquid.

Twyman and Hitchen (1931*a*) in the quantitative analysis of solutions containing mixtures of cobalt, nickel, chromium, and iron found that Hartley's form of sparking tube, and also the modification used later by Pollok and Leonard, suffered from the defect that, owing to incrustation of the electrodes and to decomposition of the solution around them, the spark soon became unrepresentative of the bulk of the solution. Duffendack, Wiley and Owens (1935)—see also Duffendack and Thomson (1936)—describe an improved form of this tube.

The latest form of sparking tube used in my laboratory is illustrated in Fig. 28. The spark gap is formed by two graphite electrodes A with flat ends 5 mm. in diameter. They fit well the glass tubes B_1 and B_2, and are kept in position by rubber tubes C_1, C_2, C_3. The solution to be analysed enters the spark through the channel D in the lower electrode. The container E is well above the spark level and has a large diameter, so that during the exposure the level difference between the spark and the surface of the liquid in the container remains practically constant. The surface of the inner part of the tap F is provided with special channels which allow the tap to be set for a certain running speed without its position being very critical. The tap can be closed, set for the running speed chosen, or left fully open, at will. The tube G, which has an aperture for the passage of ultra-violet rays, prevents dissemination of spray. The glass tube B_1 containing the lower electrode is fitted to the sparking tube by means of the ground joint H and is held by the elastic band I. The tube B_2

containing the upper electrode is kept in position by the lid *K*, to which it is attached. The two rubber-covered tubes B_1 and B_2 allow the sparking tube to be fitted easily to the spark stand, contact being made by special wires. The graphite electrodes, after having been rinsed, can be used again, since compared with the rather large quantity of solution running through during one exposure (2 to 4 ml.) the quantities of the previous solutions which may remain after the rinsing are negligible.

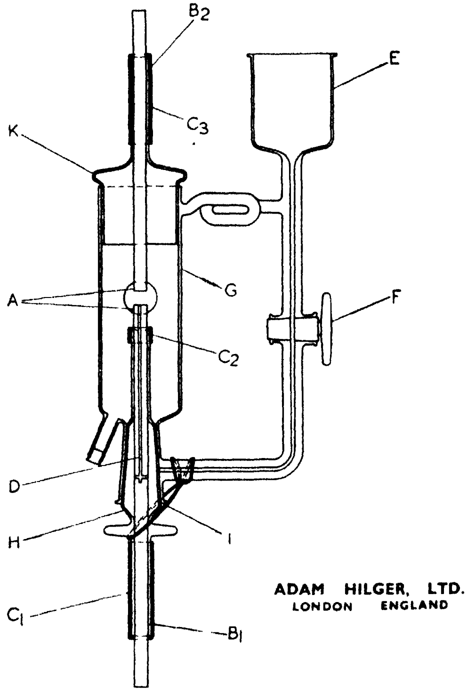


Fig. 28.—Sparking Tube for Liquids.

The tube gives very high intensities (especially if combined with the tandem spark, § 89) and constant sparking conditions. It is mechanically strong, and has no parts liable to break down under the influence of high voltage or heat.

Another method for the analysis of liquid specimens is that described by Loewe (1928). Carbon electrodes are used, a drop of the liquid is placed (by means of a pipette or glass tube) in a cavity in the lower electrode, and the spark is passed. The reference contains reproductions of the spark spectra of solutions of salts (mostly chlorides) containing the elements in the following concentrations: 1, 0·1, 0·01, and 0·001 per cent. The spark spectrum of the carbon electrodes is also included for comparison. Thus, by comparing the spectra photographed with those reproduced in the reference an estimate can be made of the quantities of the elements present. It is, of course, desirable that the carbon electrodes should be of the highest purity, and that before use these electrodes should be examined spectrographically to check the purity. If samples are dissolved in reagents before the analysis is made, the adequate purity of these reagents should also be ascertained by spectrographic test. The method has since been used by Nitchie and others (§ 125).

De Gramont (1907) used a method for obtaining the spark spectra of solutions free from lines due to metallic electrodes. The spark was made to pass between two drops of the solution, the drops being formed at the ends of quartz capillary tubes, which dipped into separate reservoirs of the solution.

Still another method of dealing with liquids is that of Lundegårdh (1934), who designed an electrode holder in which the pair of electrodes is periodically dipped into the liquid to be analysed, no current passing from electrode to electrode during their immersion, and the electrodes being of pure carbon.

Gerlach and Schweitzer (1931*a*) use a circular metal dish 10 mm. thick and having a spherical concavity 2 mm. deep and 45 mm. in diameter. The cavity is thickly gilded or lined with platinum foil, and is filled with the solution to be tested until the meniscus of the liquid stands 1 to 2 mm. above the level of the periphery of the dish. The latter is accommodated in the lower holder of the spark stand. With this arrangement it is stated that the spark may be passed with much greater energy and without any appreciable amount of spraying from the liquid surface opposite the solid electrode, where the spark spreads out to the extent of a few millimetres into a vigorously oscillating aureole. The rate of volatilization in the spark itself is very great.

§ 92. Sections of Plant or Animal Tissues and the like.—For the examination of biological sections Gerlach used the high-frequency spark mentioned *above*, as this can be applied to any point of the section with almost microscopic accuracy. The holder for the specimen is shown in Fig. 29. Gerlach and Gerlach (1934) say (*translation*):

"For the plate electrode of the spark gap for the analysis we take an aluminium plate *E* a few millimetres thick. On this is laid a glass slide *G*, 9 cm. × 12 cm. and 0·5 mm. thick, which extends slightly beyond the aluminium plate as a safeguard in case the spark should strike sideways. The thin glass slide is made to adhere firmly to the aluminium plate with the help of a few drops of glycerin. On top of the glass is laid a good-quality filter-paper *F*, about 3 cm. × 6 cm. in size, moistened with 10 per cent. sodium nitrate solution. The organic preparation *P*, or the filter with the deposit which it is required to analyse, is then laid on the filter *F*. As both preparation and filter become heated during the passage of the spark, a sufficient quantity of 10 per cent. sodium nitrate solution is dripped on to them during the taking of the spectrogram to prevent combustion with an actual flame. It is important not to give too much of the sodium nitrate solution, because complete combustion, which is the aim, is naturally attained more quickly if the preparation is kept as dry as possible, and in this way it is also more effective. The aluminium plate rests in a ball and socket joint *K*, and it and the preparation can therefore be turned and moved about during the taking of the spectrogram. The supporting rod for the ball

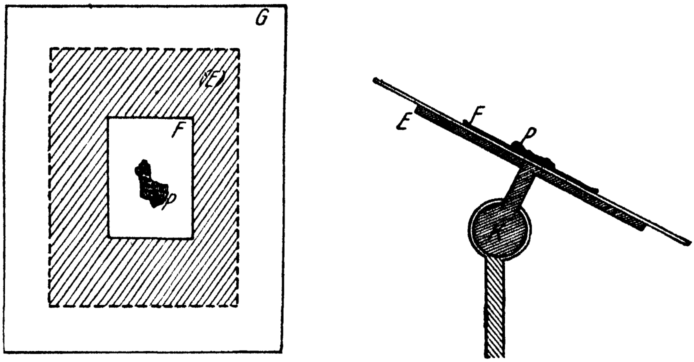


Fig. 29.

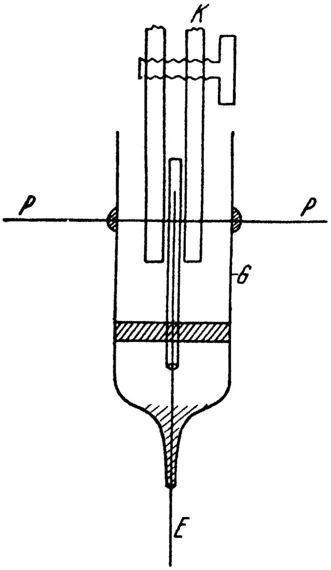


Fig. 30.

and socket joint is part of the spark stand, as is the second electrode.

"The second electrode is shown in Fig. 30. The metal for this is not a matter of importance. Gold or platinum wire is preferable, comparative purity being possible, while these metals will not oxidize during the passage of the spark and are easy to purify. The wire *E* is cemented into a glass protecting tube *G* with picein ; the glass tube is drawn out at the end into a fine capillary, so that the wire fills it practically completely. At its upper end the wire *E* is soldered to a thicker wire of copper, which is held in *G* by a cork. The copper wire is held in the clamp *K* of the spark stand. For further security we also surround the protecting tube *G* by a large plate *P* of mica. It has proved advisable to select for the electrode *E* thin wire of about 0·2 to 0·6 mm. diameter, as the spark is then more constant, and the spectrum of the electrode appears more faintly."

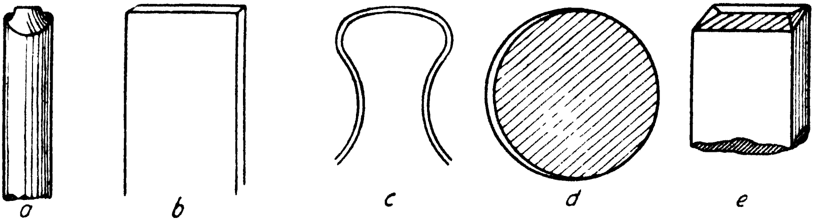


Fig. 31.

§ 93. Gerlach's Recommendations concerning Sparking Electrodes.—Gerlach and Schweitzer (1931*a*, p. 38) recommend a number of different shapes of electrode designed to give effect to the conditions they consider desirable, which are :

(1) The spark should oscillate exclusively in the direction of the optic axis.

(2) The surfaces taking part in the spark discharge should not become unduly heated (*i.e.* the spark must not be allowed to pass continuously between the same points).

(3) The electrodes should be such that they may be conveniently produced from the available material. Incidentally, it should be practicable to satisfy the further condition that little or no material is to be wasted.

Fig. 31 shows electrodes of different shapes recommended by Gerlach, the upper end of the sketches in every case representing that from which the spark emanates. Thick wires, he says, should be cut off with pliers (*a*), sheets cut into rectangles (*b*), thin wires bent into loops (*c*), and thick cylindrical rods cut into discs (*d*). Bars and blocks may be made to furnish suitable electrodes by cutting off specimens of the kind shown at (*e*). The electrode surfaces should be free from points and jags, and should be as smooth as possible. Failing this, the spark attaches itself to these points, and gives rise to local heating. The conditions under which the discharge takes place thereby lose their constancy, band spectra arise in greater intensity, and the intensity of the air lines is liable to vary, so that it is often impossible to distinguish air lines from the lines of an admixture in the electrode, especially in qualitative analysis. Finally, it may easily happen in these circumstances that volatile associated substances are distilled out, in consequence of which the intensity of the spectrum lines might greatly exceed that conforming to the actual concentration. All these contingencies should be rigorously taken into account where a special analytical investigation does not admit of the choice of one of the electrode forms *a*-*e* (Fig. 31), and where, for instance, jagged fractures are to be subjected to analysis.

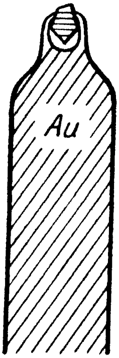
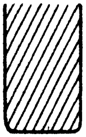


Fig. 32.

The length of the electrode surface is in itself a matter of no moment. Where the specimens admit of it, lengths ranging from 3 to 10 mm. may be taken. The distance between the electrodes (*i.e.* the spark gap) is usually about 2 to 3 mm.

The manner in which minute specimens may be employed may be illustrated by the following example: A wire of very pure gold of a thickness of a few millimetres should be excavated at the end in the manner shown in Fig. 32. It should then be provisionally thoroughly sparked in order to remove any contamination occasioned by contact with working tools (notably steel). The cavity should then be made to receive the very small specimen, which is burnished in the electrode as is a mounted jewel. The opposite electrode should likewise be of purest gold. The spark will then pass directly over to the point of the specimen. The reason why gold should be chosen as a mounting medium is that the vapour pressure of the latter should, where at all practicable, be less than that of the mounted specimen.

Very small quantities of metallic powder or traces of metallic mud (and also dissociable traces of a metal salt) should be moistened, and rubbed down with very little filter-paper, after which a pellet should be made of it, which should be thrust into a glass tube slipped over the lower electrode in the manner shown in Fig. 32A (*cf.* § 115). In some cases it is expedient to add to the water used in the preparation of the pellet a trace of sodium chloride in order to increase the conductivity. In other cases the metallic powder may, by way of example, be fused into cadmium.



In some cases it is desirable to let the spark discharges take place in an atmosphere of a neutral gas instead of in air ; Gerlach describes a simple way of effecting this, in which the spark takes place in a blown glass vessel with a quartz window for the emission of the radiation (Fig. 33). The electrode holders are movably attached by means of air-tight rubber sleeves to glass arms of the vessel on either side. The gas enters through a glass tube and streams directly upon the middle of the spark gap, cooling the electrodes as a result of its continual and rapid renewal.

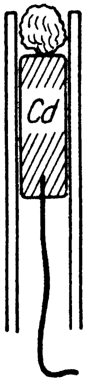


Fig. 32A.

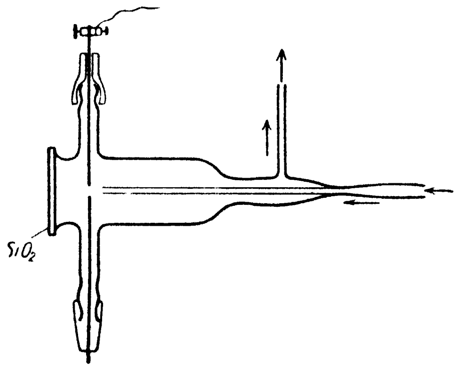


Fig. 33.

The above recommendations of Gerlach's have value as the conclusions of one who has attacked many problems in the field of spectrochemical analysis and to whose activities much of the recent rapid progress has been due. The metallurgical laboratories in various parts of the world, and their advisers, have, however, in the last few years standardized routines appropriate to their individual problems, and these are dealt with in Chapter IX.

Preliminary Treatment of Specimens.

Although the ways of exciting emission spectra already described usually suffice, the sensitiveness and certainty of spectrochemical analysis can often be increased by appropriate preliminary treatment of the specimens, and a few devices of the kind (of wide application) will now be referred to.

§ 94. Preliminary Chemical Separation.—When extremely minute portions of an element are of interest, and when the main constituents of the specimen have complex spectra, it may be worth while effecting a preliminary chemical separation so as to remove the main bulk of the major constituents, and to concentrate the remainder. Spectrographic examination is then made for the elements in the chemical groups which would contain the elements of interest.

Such a procedure, which may enhance many times the sensitivity of the method, is more likely to be necessary when the dispersion of the spectrograph is small. Thus, in analysing metals and alloys, if a large quartz spectrograph be available, it is but rarely the case that separation of any kind is necessary ; if high dispersion is not available, and if any of the metals in Table IV (§ 47) predominate, it may be well worth while to divide the complex into two or more portions chemically.

The chief provision against the necessity of having recourse to such separations is to work with the instrument in good adjustment and with a narrow slit, so as to get sharp lines distinctly separated from one another.

An important consideration is the proportion of the element present which is to be sought. When the quantity is very small, and the sensitive lines which may be expected to appear happen to be very near to lines of the dominant element, there may be some uncertainty. No hard and fast rule regarding when to employ chemical separation can be given ; and recourse to the separation need not be had unless a first search without it fails.

There are, of course, other methods of effecting separation besides chemical precipitation, and any of these methods could be employed. One that may be mentioned is that of electrolysis. In the case of solutions suspected to contain salts of mercury electrolysis of the solution by means of, say, a 6-v. battery is sufficient to effect a separation. Gold-foil electrodes should be employed, and these should then be examined spectroscopically. This method was used by Dupré for the examination of explosives as early as 1907, the examination being performed by means of a wavelength spectrometer (§ 98).

§ 95. Ashing of Specimens, etc.—In quantitative work and in those cases where a set of analyses are required to be closely comparable, if the compounds under examination are not in a similar physical and chemical condition to start with, then it is desirable to bring them into a similar condition. Judd Lewis (1936) has developed a technique for attaining this in arc spectrography, the specimens (and any standard substances that they are to be compared with) being brought into the form of sulphates. Animal or vegetable matter is first ashed to eliminate organic matter which may be present. Care must be taken to avoid the loss during the ashing of volatile constituents and of those which become volatile on reduction by heating with carbon (*e.g.* arsenic, phosphorus, zinc).

The procedure is to heat gently the mass to be analysed, from time to time moistening with concentrated nitric acid. When the ashing is complete the mass is sulphated by the addition of a few drops of concentrated sulphuric acid, and the excess sulphuric acid fumed off. Then the ash is finely powdered together with an equal mass of spectroscopically pure ammonium sulphate and finally compressed into a pellet (§ 115).

When the substances are present in the form of solution, the conditions of like state and homogeneity are easily fulfilled. It is very important that the solutions used for comparison should be very pure, but a number of spectroscopically pure salts are now on the market.

§ 96. The Exploded-wire Method for Fine Wires and Filaments.—As illustrated *above*, special methods can often be developed to meet particular cases. A further example is the problem of detecting the spectroscopically insensitive element thorium in fine wires 0·0016 cm. in diameter and a few centimetres long, the mass being of the order of 0·2 mg. Ryde (of the General Electric Company, Wembley, England) found that the thorium lines showed up more readily the greater the excitation, and adopted the method of exploding a bank of condensers (capacity up to 0·05 μf.) through the wire. Such a discharge through a wire 1·5 cm. in length proved sufficient to register the spectrum with an F_D 170 cm. quartz spectrograph, and it was found that as little as 0·02 per cent. of thorium and 0·005 per cent. of many other impurities could be detected in tungsten. Later work has shown the method to be of general use in this type of problem, whilst quantitative results are readily obtained (Smithells, 1926).

§ **97. Thin Metallic Films.**—The examination of very thin metallic films presents difficulties, but is an analysis which is called for upon occasion. It has been found in my laboratory that one method of analysing such films is to support the film in question between two electrodes, say of copper, and to pass a condensed discharge between these electrodes. The discharge removes the film, and by photographing the spectrum of the spark it is possible to determine the nature of the film (Harvey and Dreblow, 1933).

§ **98. Detection of Mercury.**—Early in the present century trouble was caused in the testing of explosives by the presence of mercury in very minute quantities. A method for the detection of this element was accordingly worked out by Dupré (1907). The material to be examined is placed in a special discharge vessel consisting of two stoppered tubes connected by a capillary tube, and the apparatus is evacuated by means of an oil-pump. The discharge tube is then placed in hot water, and a spark discharge passed. The presence of mercury is ascertained by means of the visible lines, so that a visual instrument may be employed. It should be pointed out, however, that the apparatus itself should be carefully examined for mercury before any test is carried out.

As described *above*, by the use of electrolysis still greater sensitiveness was attained by Dupré (§ 94).

Relative Advantages of Arc and Spark.

§ **99.** For the modern quantitative methods of analysing metals and alloys the spark is almost always used. For substances not in the metallic condition and for estimating minute percentages the arc is on the whole more useful.

The arc is very convenient in practice, and more sensitive than the spark. The following comparison will indicate which is the better to use in a given problem. One notable difference is that an arc consumes more of the electrode material than does a spark. Thus, on the one hand the former gives more reliable knowledge of the average composition, while on the other it is not applicable when the specimen must remain undamaged. A spark may seek out points on the electrode where materials may exist in small inclusions, whereas an arc strikes to a considerable fraction of the surface of the ends of the electrodes; yet if the material is thoroughly homogeneous the spark seems to give a truer representation of the contents of the specimen. The very high temperature of the electrodes gives a high concentration of vapour in the arc, and to this its sensitiveness is probably due. This high temperature also renders the arc effective in dealing with substances such as glasses, slags, etc. When D.C. is available the arc possesses a notable advantage over the spark as regards the simplicity of the equipment required.

It should be observed that the spark discharge is generally more constant in position and character. One consequence of this is that it gives a more constant illumination on the spectrograph slit than the arc. With easily oxidizable or low melting-point metals and alloys and in certain other cases (*e.g.* nickel in iron) it is sometimes particularly difficult to obtain an arc discharge which is steady either in position or character. On occasion, with the arc in this unsteady state, certain lines can be observed to fluctuate in intensity with respect to one another. The irregularities in the character of the arc can be largely cut out by the introduction of a self-induction of, say, 0·3 H. in series with the arc ; but this does not make the arc any steadier in position.

It is well known that the condensed spark will bring out lines of many of the non-metals as well as of the metals. Little practical use has been made of this except with regard to arsenic, boron, carbon, phosphorus, antimony, silicon, and tellurium, which de Gramont found in fused salts, minerals, and alloys. It is not so well known that all of these except tellurium (which we do not know to have been tried) are excited by the arc. As regards their sensitivity in the arc, silicon, antimony, and boron show up with moderately small quantities, but the spark may be better if the highest sensitivity is required. Thus, the silicon line at 3905·7 A. and the carbon line at 2478 A. are both fairly sensitive in the spark, and can be used for the quantitative determination of these substances when present in steel.

One drawback to the use of the spark is the noise associated with it. It has been found in my laboratory that this can be almost eliminated by putting the spark within a suitable enclosure. A large box made of corrugated cardboard, within which there is room for the Gramont arc and spark stand, has proved fairly effective. The lens is mounted in a small opening in the box ; of course, should no lens be employed, then the aperture should be closed by means of a plate of glass or quartz.

For the use of the spark in specific methods see Chapters VII and IX.

CHAPTER VI.

TAKING SPECTROGRAMS, MEASURING WAVELENGTHS, AND IDENTIFYING ELEMENTS: BOOKS AND TABLES.

§ 100. Lining up the Light-source.—The spectrograph having been placed in position, and any instructions issued by the makers having been complied with, the first thing to do is to line up the light-source. Possibly the means of doing this have been provided by the makers ; in any case the following way of checking the alignment should be known :

To set up the source of radiation, as for instance an arc, it is placed in line with the collimator at the correct distance from the slit. The light-source is then moved slightly perpendicularly to the axis of the collimator, until a position is found by trial and error such that on looking through the spectroscope or spectrograph (using a wide slit and in the former case removing the eyepiece) the trace of the flame, arc, or spark is seen in the middle of the prism aperture.* To use the form of illumination (*i*) (§ 54) the condensing lens is then put in and an image of the light focussed on the slit. Once the correct position of the condensing lens has been found, it should be left so, all future adjustments to bring the image of the light-source on to the slit being made by moving the light-source. On again looking through the instrument the whole aperture of the prism should be illuminated, when the adjustment is complete.

If form of illumination (*ii*) (§ 54) is wanted, the condenser is put at the right distance from the slit for that position, and moved until, looking in at the camera, an image of the arc is seen in the middle of the prism aperture. The slit should then be closed to the desired width.

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* Occasions may arise when it is desirable not to strike the arc until the actual exposure is made. In such cases one may place a frosted lamp in front of the slit at a distance greater than that of the arc. Looking in the camera the surface of this lamp is visible ; the arc is then moved across the lamp until the poles of the electrodes are visible, silhouetted against the lamp and situated centrally in the field, when they will be in the correct position.

To get the fullest illumination of type (*i*) for any part of the spectrum there is a best position for the condenser, and although no very great accuracy is needed in this adjustment, it is worth while to have a note of the best distances between slit, condenser, and light-source for the visible, and for one or two wavelengths in the ultra-violet.

§ 101. Taking Spectrograms.—The foregoing adjustments having been completed, a photographic plate is put into the plateholder, which is then placed in position in the spectrograph. The shutter of the plateholder is withdrawn, the slit shutter being closed. The source of light (arc, spark, or flame) is started, and the exposure continued for from 3 to 60 seconds or more, according to the nature of the light-source, the region of the spectrum to be studied, the width of slit, and the purpose in view. Guidance on this point will be found in the specific instances mentioned in Chapter IX.

It is usual to take a number of spectrograms on one plate, by raising or lowering the plateholder after each exposure has been completed.

Choice of a Photographic Plate.—This is considered in Chapter IV (§§ 61 to 62. 1).

§ 102. Interpreting Spectrograms.—Before discussing the interpretation of spectrograms there are certain phenomena which must be mentioned :

At times the observer finds on his spectrogram a very large number of lines so closely packed together as to present the appearance almost of a continuous background, often of a " fluted " character. These are caused by molecules ; for example, an arc between aluminium electrodes gives the aluminium-oxide spectrum, copper electrodes give the copper-oxide spectrum, and graphite and carbon electrodes give the cyanogen spectrum. Such spectra are known as *band spectra* and, most frequently, are nothing but a nuisance to the analyst. Occasionally, however, the bands are so distinctive as to form the readiest indication of the presence of any considerable quantity of a material ; this is so in the case of fluorine, for instance. Ordinarily, however, these masses of fine lines are useless for the identification of elements.

Many strong lines will be found to possess a shading or fringe on one side. When the instrument is well adjusted, and the circumstances favourable, this shading resolves itself into a number of fine lines. These lines are not used in spectrochemical analysis, and they are mentioned here merely as a warning to those whose attention may be distracted by their presence.

To proceed now to the subject of interpreting spectrograms: The questions the chemist may refer to the spectrograph are broadly divisible into three classes:

(i) Does a substance contain a given element?
(ii) What are the elements present in a given substance?
(iii) What percentage is present?

We shall here consider a typical procedure for each of the first two cases—the answer to the third is to be found in Chapters IV, VIII, and IX.

§ 103. (i) To ascertain whether a Substance contains a Specified Metal.—In front of the slit is a sliding plate pierced with a number of holes (three is a common number), each covering only a part of the slit, and so staggered that one only can be brought in front of the slit at a time, thus producing contiguous spectra. This is known as a Hartmann diaphragm. With the bottom hole in position take a spectrogram of any metal M_1 (in the purest form obtainable) which is known to be present in considerable quantity. Without moving the plateholder or shutter of the camera, and with the middle hole in position, take a spectrogram of the specimen under test. Again, with the top hole in position, and without moving plateholder or shutter, take a spectrogram of the metal M_2 whose presence or absence is to be determined. The first photograph shows which lines in the middle photograph can be ignored as being due to the metal M_1, already known to be present; the third enables one to tell at once whether M_2 is present or not.

It should be remembered that it is the top aperture of the Hartmann diaphragm which gives rise to the bottom spectrum on the plate.

If examinations for the presence of other metals require to be made on the same specimen, or if other specimens are to be tested, the same plate can be used by racking the plateholder to a fresh position. Each set of photographs will then on development appear as in Fig. 34, where the bottom spectrum is of zinc supposed to be pure, the middle is of a sample of zinc spelter under examination, and the top is of cadmium, the metal whose presence or absence is to be determined. By seeking in the middle spectrum lines which are absent from the bottom, but strongly present in the top, one finds through the presence of the sensitive cadmium lines 3261·1, 3403·6, 3466·2, and 3610·5 A. that the spelter contains some cadmium. The two lines 3247·5 and 3274·0 A., which appear in all three spectra, are the *raies ultimes* of copper, showing that even the supposedly pure zinc is not free from a small quantity of this impurity. Lead is present in both the cadmium and spelter, but not in the pure zinc, as shown by the lines 3683·5 and 3639·6 A. A small quantity of silver is present in all three samples. The silver line 3382·9 A. appears faintly in the three spectra, but the line 3280·7, which is present in the spectrum of the cadmium, is masked by the strong zinc line 3282·3 in the two zinc spectra.

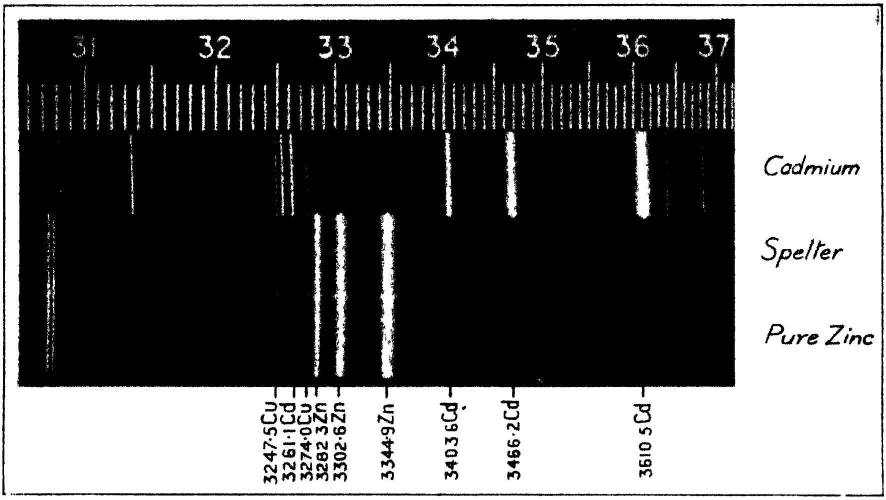

Fig. 34.—Set of Spectra obtained with a Hartmann Diaphragm.

§ 104. (ii) To determine all the Metals present in a Specimen.—(*a*) A set of photographs is taken as described in § 103, the top spectrum (obtained through the bottom aperture of a Hartmann diaphragm) being that of iron or copper.*

The wavelength of each unknown line must then be measured in the following way:

Choose two neighbouring iron lines, *A* of smaller wavelength and *B* of greater wavelength, lying on each side of the unknown line *C*, and the nearer the better. Such lines are shown in Fig. 35. Ascertain the wavelengths of the iron lines *A* and *B* by reference to an enlargement of the iron arc spectrum marked with wavelengths.

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* The method of simple linear interpolation here described is, in the case of prism spectrographs, only applicable over narrow ranges (§ 71).

The descriptions of this and the following methods are given for the sake of completeness, but there are few occasions when they cannot be avoided by the use of comparison spectra of the metals known to be present in the specimen.

At this stage the spectroscopist will be able, in the great majority of instances, to state to what metal the unknown line is due ; but failing the necessary experience the procedure is as follows :

Measure on a micrometer* the distances *AB* and *AC* (Fig. 35). Suppose these distances are 5·301 and 3·090 mm. respectively ; then the wavelength of the unknown line is approximately

$$5260{\cdot}33 + (5362{\cdot}45 - 5260{\cdot}33) \times \frac{3{\cdot}090}{5{\cdot}301} = 5319{\cdot}86 \text{ A.}$$

Having found the wavelengths of a number of the unknown lines in this way, reference to suitable tables of wavelengths will enable the corresponding metals to be identified.

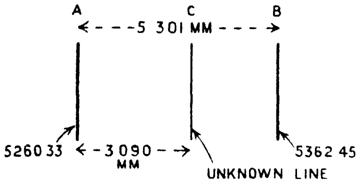

Fig. 35.

When one or more of the constituents have been determined, a second photograph can be taken in which the bottom spectrum is that of the constituents thus found, photographed one after the other without moving the photographic plate, and further search can be made for lines which are still present in the sample but are not in the comparison spectrum.

§ 105. (*b*) A method of determination which avoids the arithmetical work of interpolation is to prepare a series of standard slides in which an electrode of constant kind is used, arranging the spectrograms as in Fig. 36, and using them as follows :

One must first decide with what kind of electrodes one will work ; carbon, graphite, copper, silver, etc., or, when, for example, steels are under examination, iron electrodes may be used.

A spectrogram is then prepared as illustrated in Fig. 36 for each element likely to be sought, *e.g.* calcium, lead, antimony, potassium, silicon, etc.

Using the micrometer, one selects any unknown line in the spectrum under study, and by the wavelength scale (if one is available) ascertains its wavelength approximately. It may be found, for example, that it is in the neighbourhood of 3965 A., and that another unknown line of similar strength occurs near 3930 A. Reference to the tables will suggest the calcium lines 3968·48 and 3933·67 A. as the most probable. By the micrometer it is found that the first unknown line is, say, 1·057 mm. from the 3977·746-A. iron line, if iron electrodes are used, and that the second line is 3·724 mm. away from the same iron line. On comparing this with the calcium standard, identical measurements may be observed, when the presence of the element will be verified. In the event of the speculation as to the element concerned being wrong, the effort has not been wasted, for from the differences in the micrometer readings one will get at once a close indication of the true wavelengths.

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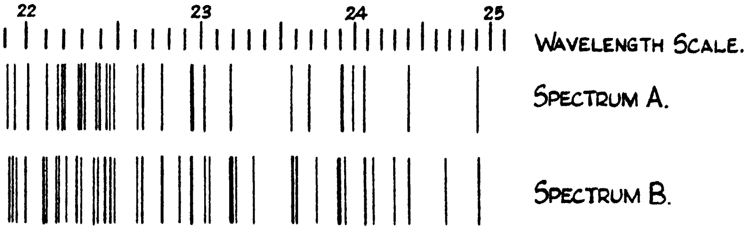
* The micrometer as an instrument by itself is now rapidly being replaced by the addition of a fine screw motion on the microphotometer, or by the use of a fine scale with one of the forms of projection comparator (§ 105).

A great saving of labour is achieved if a spectrum comparator is used in place of the micrometer referred to in the last paragraph. By means of this instrument the images of two spectrograms on different plates may be brought into juxtaposition, either in an eyepiece or by projection, so that the image seen with spectra photographed on separate plates and viewed through the comparator is precisely similar to that of two spectra produced through adjacent apertures of a Hartmann diaphragm on one plate. Hence, given a set of reference plates (which can gradually be built up by the user) the need for taking comparison spectra of metals looked for against that of the unknown is obviated. A great deal of tedious measurement is likewise eliminated.



A Spectrogram of the electrodes alone.
B Composite spectrogram of the electrodes and the selected metal.

Fig. 36.

§ 106. (*c*) Some makers provide a spectrum enlarger, in which an enlarged image of the plate under examination is projected on to a screen, comparison then being made with enlarged prints of spectra of the various elements sought.

It will be seen that method (i), *above* (§ 103), by using a comparison spectrum of the particular element of which the presence or absence in the sample is required to be determined, obviates entirely the determination of wavelengths. In cases where it is desired to analyse completely a complex material, method (i) is inconvenient because a large number of spectra have to be taken. In such cases a spectrum comparator is invaluable.

§ 106.1. It is not essential, however, to have a complete comparison spectrum of an element in order to identify it in the sample. All that is necessary is that the comparison should show the most important sensitive lines of the element, since if these are not present in the spectrum of the sample, then none of the less sensitive lines will be. The ideal comparison spectrum is thus one in which the most sensitive lines of all the elements appear, provided the number due to each element is sufficiently small to prevent confusion and large enough to allow confirmations to be made. Such a comparison spectrum can now be bought, together with a powder consisting of mixed salts, spectra of which can be photographed with the carbon or graphite arc.

One such powder has been developed by Ryde and Jenkins at the Research Laboratories of the General Electric Company, Ltd., Wembley, England, and called by them the " R.U. powder." It consists of small quantities of fifty elements incorporated in a base material composed of zinc, magnesium, and calcium oxides. The quantity of each element present has been carefully adjusted so that only the *raies ultimes* and the most important sensitive lines appear when the spectrum is excited by placing some of the powder on the lower (and positive) pole of an arc between graphite electrodes.* A current of not less than 5½ amp. should be used. On the average, about seven lines appear per element. All the elements present are evenly distributed throughout the bulk of the powder, so that, under controlled conditions of excitation, the same composite spectrum is always produced.

When used as a comparison spectrum, the sensitive lines of all the elements present as impurities in the substance under examination will coincide with the corresponding lines in the R.U. spectrum. A set of enlargements of the arc spectrum of the R.U.

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* The experience in the G.E.C. Research Laboratories is that in using the powder it is better to put the positive electrode at the bottom. When this is done the lines of the R.U. powder show more continuously in the spectrum than if the negative electrode is at the bottom. The greater continuity of the R.U. spectrum can be confirmed by simple observation of the arc itself; the R.U. powder communicates a green coloration to the arc, and this is found to be less subject to fluctuation when the positive electrode is at the bottom. It should be noted that the R.U. powder cannot be used to full advantage with alternating current.

powder has been prepared, and the origin of each line is marked, so that all the elements present in the sample can be readily identified.

The groups of lines mentioned *below* (§ 106. 2), which are highly characteristic of each element, as a matter of course appear in the R.U. spectrum, and after a little practice can be recognized at sight.

The R.U. powder, owing to its complex spectrum, is suitable only for use with high dispersion. A similar purpose can be fulfilled with less powerful instruments by the use of simpler mixtures.

§ 106. 2. In conclusion, it should be noted that in addition to these procedures, there is another method, which, with experience, soon becomes of great value. In every spectrum there are groups of lines which are highly characteristic of the metal, and these become familiar and recognizable at a glance by those making frequent use of the spectrograph.

It is worth remembering that this ease of recognition depends somewhat on there being a constant ratio between the height of the spectrum band normally recorded and the separation of certain pairs of lines. Illustrations of spectra are confusing if this ratio is not constant, and still more so if the wavelength increases to the left instead of to the right, if one is accustomed to the latter.

BOOKS.

§ 107. There are not many good books on spectrochemical analysis, and the subject has been developing so quickly that such books as have appeared have rapidly become out-of-date. A book written before 1935 may be worth reading as an introduction to the subject, or to a particular branch of it, or as an account of the work of some outstanding investigator, but it cannot be a guide to the technique of spectrochemical methods as now practised.

Most of the books have indeed been written by workers who have developed very completely some line of investigation of their own ; references to these will be found in appropriate places in this book.

My own *Practice of Spectrum Analysis* (1935) and *Spectrochemical Analysis in 1938* (1938) were, I hope, useful at their respective dates, but all that is of permanent value in them can be found in this book.

A good and readable introduction to the subject is Judd Lewis's

Spectroscopy in Science and Industry (1936). It is short and simple, and deals also with absorption spectrophotometry. It can be strongly recommended as a preliminary introduction to the subject.

La Spectroscopie appliquée, by P. Swings (1935), in French, is also a good introduction to the subject, and deals briefly with absorption spectrophotometry.

Foundations and Methods of Chemical Analysis by the Emission Spectrum, by Gerlach and Schweitzer (1931*a*), reviews the subject as developed up to the date of publication. Gerlach and Schweitzer are among the leading European workers responsible for the development of the subject from 1926 onwards, and the results of their work are well set forth. A second part of the same work, by Walther and Werner Gerlach (1934), deals primarily with clinical and pathological applications of the methods, but also includes much general information useful to the spectroscopist.

Two other German authors, Henrici and Scheibe (1939), have produced a small monograph, *Chemische Spektralanalyse*, which summarizes the progress of the subject between 1933 and 1938; the book treats light-sources and quantitative procedures at great length, and contains an excellent bibliography covering the years 1932-37 with very brief abstracts of each paper.

The most up-to-date general work on the subject is the American *Chemical Spectroscopy*, by W. R. Brode (1939), which covers a wider field than that of emission spectra only, but is sufficiently detailed to give a clear view of the scope and technique of spectrochemical analysis. The book contains an excellent selected bibliography of both monographs and papers.

A book of a different character is *Chemische Spektralanalyse*, by Seith and Ruthardt (1938). This is admirably arranged as a handbook for a laboratory class. The progressive experiments described are excellently set out, and selected so that the student having passed through them would have acquired a good practical acquaintance with the subject. It suffers from one serious fault—references to work done outside Germany are very inadequate.

Bibliographies of the subject have recently become available which enable any specialist to look up the relevant research papers quite easily. The largest is that of Meggers and Scribner (1939), which covers the years 1920-37 with entries of about 900 references. The next in time and bulk is the work by Scheibe and Henrici (1939), which contains about two-thirds as many references covering the period up to 1938, adequately indexed with cross-references.

My own *Spectrochemical Abstracts, 1933-37* (1938*a*) is very complete within its range, and I personally find the arrangement which I adopted extremely convenient for reference, and the abstracts adequate for many purposes. A second booklet of *Spectrochemical Abstracts* is being edited by E. van Someren, who has long experience both of analysis and of abstracting in this field. It will cover the papers published in 1938-39 with a system of indexing under subjects and under authors similar to that used in the first volume.

Other collections of abstracts are published by the British Non-ferrous Metals Research Association from time to time. For reviewing current work recourse must be had to the annual subject indexes of *Chemical Abstracts*, *British Chemical Abstracts*, or of metallurgical abstracts, cautiously looking up in turn " Analysis, Methods of," " Spectrographic," and " Spectroscopic " as key words, since the terminology of indexes is liable to variation from year to year.

In 1939 there appeared for the first time a periodical devoted to research on spectrochemical analysis, which was published in Berlin and edited by a small committee of five authorities working in four countries. *Spectrochimica Acta* contains in its first three issues a score of important contributions on the principles and technique of spectrochemical analysis in English, French, and German. The war has interrupted the co-operation of the editors, but the review still appears from time to time. The book-review and abstract section was good in quality but inadequate to cover the field.

TABLES AND CHARTS.

§ 108. The spectroscopist requires to draw on the experience of others for tables and charts of spectra, which correspond to directories and maps as keys to industrial life. Tables, like directories, are never quite up-to-date and never infallible, and their errors cause a great deal of inconvenience. There are two kinds of tables, classifying lines in order of wavelength or according to their origin. The former are more generally useful, but are never complete ; consequently tables of all the lines attributed to each element must occasionally be consulted for purposes of quantitative analysis.

The most generally useful book of wavelength tables is the *Tabelle der Hauptlinien* compiled by Kayser (1939), which contains a selection of lines sufficient for nearly all analytical problems. It is a handy book with wide margins in which one can make notes.

When this book fails one may refer to the great new book published by the Massachusetts Institute of Technology, *Tables of the 100,000 Principal Spectrum Lines* (Harrison, 1939), which makes a wider selection of the known spectrum lines, and includes many revised measurements. These tables also include a table of 500 of the most sensitive lines of the elements, arranged under the elements and also by wavelengths ; tables of this kind are indispensable for qualitative analysis.

Several shorter sets of tables of the most sensitive lines are available, such as *Wave-length Tables for Spectrum Analysis*, by Twyman and Smith (1931), which summarizes the knowledge then available about the most persistent spectrum lines of the metallic elements in arc, spark, and sometimes flame spectra. A very similar set of tables, somewhat amplified and revised, but not perfected, is appended to *Chemical Spectroscopy* (Brode, 1939), where they are followed by a more generous selection of lines filling a hundred pages, with tables of the more important lines of each element. For quantitative analysis one also needs to know which lines have been found useful for intensity comparisons, and notes summarizing the results published by various workers in this connection are included in Brode's tables. The value of the spectroscopic data collected by Brode in his book is such that most practising spectrographers should buy it for these alone, whether or not they require it as a textbook.

The identification of spectrum lines by means of tables is sometimes difficult, and the tables published by Gerlach and Riedl (1936) as volume 3 of *Die chemische Emissionsspektralanalyse* are compiled to simplify this task. These tables cover the most persistent lines of 57 elements, tabulating for each element a list of the other elements which might provide coincidences with each sensitive line, and also other lines which do not coincide but lie close enough to cause possible confusion. Besides this the authors list control lines, which are lines whose intensity relative to that of the sensitive line gives evidence as to whether or not a coincidence of lines has occurred. These tables are extremely helpful, especially to anyone who uses them habitually. The system of presenting the information is so compressed that the abbreviations necessary may confuse the occasional student. Some of the information about control lines has been incorporated into Brode's tables.

Spectral charts are simply enlarged diagrams or photographs with the wavelengths and identities of the lines indicated beside the illustration. They are tempting to the beginner because they are more graphic than tables of lines, but they are best used as time-saving accessories to tables rather than by themselves. Charts are usually photographs, and one of the most useful is the set of enlargements of the spectrum of the R.U. powder (Ryde and Jenkins, 1929), which shows the position of the sensitive lines of 50 elements in the arc spectrum relative to an iron spectrum (§ 106. 1). A set of diagrams of spectra of similar scope has recently been published in Chicago (Pierce, Torres and Marshall, 1939), in which the position of the sensitive lines is indicated on cards, next to a diagram of the iron arc spectrum. These cards are intended for use under a projector or enlarger, by which the spectrum to be analysed is projected on to the card, and an adjacent iron spectrum is fitted to that on the card to secure identity of scale and positioning.

Another set of spectral charts intended to be used in this way is incorporated as 35 plates in Brode's book, where a strip of iron arc spectrum photograph is printed adjacent to a blank space, at the edge of which the position of the lines of other elements is indicated. Such charts are very helpful, if precautions are taken to make the iron arc exposures under the right conditions.

The iron spectrum, whose wavelengths have been measured with great precision, is frequently used as a comparison spectrum from which wavelengths can be measured by interpolation. For this purpose photographic enlargements of the iron arc spectrum with the wavelengths indicated have been published by Adam Hilger, Ltd., and others of the arc and spark by the Astrophysical Laboratory of the Vatican (Gatterer and Junkes, 1935). In the latter set three different exposures appear on the photographs, so that strong lines can be measured from a reduced exposure with greater accuracy. Neither set is made from spectroscopically pure iron, which has only recently been produced.

An extensive descriptive bibliography of tables and charts is given in *Chemical Spectroscopy* (Brode, 1939).

There are two difficulties involved in the use of tables and charts of which the spectroscopist should be warned. The first is in the use of charts, that different illustrations of spectra naturally use different heights of the spectrum band, corresponding to different lengths of slit on the spectrograph. The visual estimate of the distance between two spectrum lines is unconsciously referred to the height of the spectrum as unit, and when spectra on a plate are being compared with illustrations in a book the visual impressions may be confusing. This can be overcome by projecting the spectra in an enlarger on to a strip of card so as to match the published charts, but this is not always convenient, and many workers feel more confidence in the examination of faint lines when they are looking at them through an eyepiece than when projecting them on to a screen.

The spectrochemical analyst often has difficulty in distinguishing the faint lines of the spectrum of an element from the moderately persistent lines of an impurity or minor constituent, and this difficulty is accentuated by the fact that most tables of the wavelengths of elements were prepared before spectroscopically pure metals were available. Consequently tables are not always reliable for this distinction, and the spectroscopist should combine a suspicious temperament with a wide knowledge of chemistry and metallurgy. If analysis of the electronic configuration of the element has assigned the spectrum line to certain specific changes, the probability that it is an impurity line is considerably decreased.

Finally I would recommend the spectroscopist to make his own spectrum charts, or even to map spectra on a much enlarged scale by means of a travelling microscope. Only in this way can the degree of confidence which should be attached to charts be appraised. For making enlargements of complex spectra the sharpest results are obtained by over-exposing the plate and using the process of physical development, which minimizes the grain of the plate and the halation of strong lines.

CHAPTER VII.

TECHNIQUES OF SPECTROCHEMICAL ANALYSIS.

§ 109. Introduction.—When a problem of analysis arises, appropriate selections have to be made of apparatus, and of means of causing the substance to emit radiation, determining from the photograph the elements present, and measuring the percentages in which they are present. Guidance on these points is given in previous chapters. When this selection has been made we may speak of the result as the " technique " or " method."

Very many such techniques have been put forward, and it is the purpose of this chapter to describe those which seem to have outstanding interest or usefulness.

The arrangement is more or less chronological, so that the chapter is, in a way, a continuation of Chapter I.

§ 110. Analysis of Solutions of Salts in the Spark (Hartley, 1884).—Already in 1882 Hartley had investigated the proportions of certain metals which would be evidenced in compounds by the presence of their lines in the spectrum, and had as a result estimated the amount of beryllium contained in certain cerium compounds. He preferred to work with solutions, and used the spark condensed by a Leyden jar. Further details of his technique are given in the following extract (Twyman and Smith, 1931) :

" Of all elementary substances hitherto photographed, graphite yields the simplest spectrum (' Note on Certain Photographs of the Ultra-Violet Spectra of Elementary Bodies ' [1882]). It shows lines and the edges of bands due to the air-spectrum to the number of sixty-six ; of rays assignable to carbon it contains but twelve. Graphite being an excellent conductor of electricity, electrodes are made in the simplest possible manner, by cutting plates of good Ceylon or Siberian graphite, tapering from one-fourth to one-eighth of an inch in breadth and three-eighths of an inch in length. Deep grooves or scratches are made in the sides of the lower electrode, which is inserted into the end of a small glass U-tube containing the solution. The upper pole may be of metal or of graphite, either being fused into a glass tube or held in a screw clip. Platinum terminals from the coil are connected with these. Capillary attraction keeps the lower electrode moist at its upper surface . . . Each of the two pieces of graphite should be sharpened so as to resemble a chisel, the edge of the one being exactly superposed above that of the other, while both are placed in a line with the slit; the movement of the spark is thus restricted to a direction backwards and forwards."

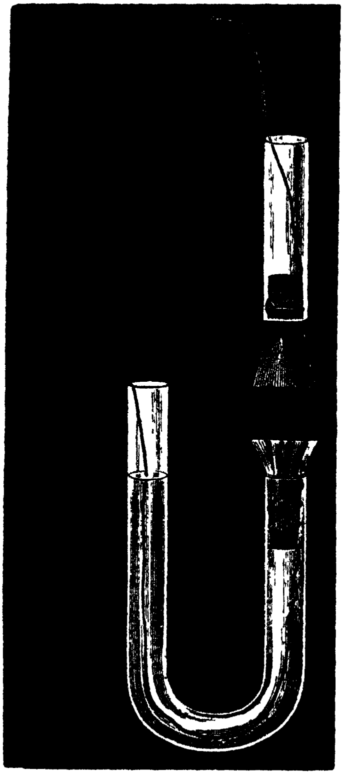


Fig. 37.—Graphite Electrodes (actual size).

The solutions were in the form of chlorides. The following are some of the conclusions arrived at by Hartley:

"When carbon or metallic electrodes are moistened the short lines are lengthened.

"With very few exceptions the non-metallic constituents of a salt do not affect the spark spectra of solutions. Insoluble and non-volatile compounds do not yield spark spectra.

"The solution of a metallic chloride yields spectral lines identical in number and position with the principal lines of the metal itself.

"The effect of diluting solutions of metallic salts is first to weaken and attenuate the metallic lines, then with a more extensive dilution to shorten them, the length of the longest and strongest lines generally decreasing until they finally disappear.

"Accidental differences in the passage of the spark or in the time of exposure of the photographic plate, when the normal period is from half a minute to five minutes, do not cause sensible variations in spectra obtained from the same substance."

The shortening of the lines referred to is seen when an image of an arc or spark is thrown on a spectrograph slit by a spherical condenser. When the condenser is used so as to make each line of uniform intensity along its length, the effect is merely that of a weakening of the line.

It was a natural development to arrange the lines of each metal in their order of disappearance and to find the amounts of each metal which, in solution, would cause these lines just to appear; and this Hartley proceeded to do. The lines which were the last to disappear were called by Hartley "the persistent lines."

Thus already in 1884 were laid the foundations of a quantitative spectrochemical analysis which, while not comparable in accuracy with that of the balance, yet in some cases gave a quick solution of problems otherwise difficult or lengthy.

As often as possible chlorides were used in preference to other salts, because hydrochloric acid is the solvent employed most generally in analytical operations, and the chlorides are as a rule the most soluble compounds of the metal and likely to yield the most concentrated solutions.

In a later paper Hartley (1884) repeats that under the same spark conditions similar solutions of the same strength always emit the same spectrum. By similar solutions are meant solutions containing salts of the same metal; for example, chlorides, nitrates, sulphates, and carbonates are specifically mentioned in this respect.

In these papers Hartley gives tables indicating the dilutions at which various lines of a number of metals are still just observable.

§ 111. Continuation of Hartley's Work (Pollok and Leonard, 1907 to 1909).—Pollok, following Hartley, used solutions, usually of chlorides. His first paper consists mainly of an "Index of the Principal Lines of the Spark-Spectra of the Elements," the lines being arranged in order of their wavelengths, but includes also the following description of the technique adopted (Twyman and Smith, 1931):

"*Analysis of Minerals.*

"To prepare minerals for spectrographic analysis they should be decomposed in the ordinary way—the solution separated into the various analytical groups, and these groups then dissolved in hydrochloric acid, or, if necessary, nitric acid, ammonia or caustic soda and made up to a fixed volume, such as 20 cc. each for every two grams of sample taken, and these solutions then sparked. If only a small quantity of an element is present, much more of the original material must be taken, and the solution made of such a strength as to contain not less than 1 per cent. of the element sought for. Iron should be separated from the ammonia precipitate by tartaric acid and sulphide of ammonia, as there are so many iron lines that it is difficult to detect other elements when it is present. A somewhat similar difficulty occurs with cerium, but cerium can be completely removed by caustic soda and chlorine.

" Silica gives no lines in an acid solution, but very characteristic lines when dissolved in caustic soda or with soluble silicates. Tungsten gives its lines when dissolved in ammonia ; the other metals may be sparked in acid solution. The non-metallic elements present do not give spectra when treated in this way ; they must be sparked in the gaseous condition, at reduced pressure, in Geissler tubes."

The chief technical alteration made by Pollok and Leonard in the apparatus was to replace the graphite electrodes by gold. This paper was followed by others all published in the *Proc. Roy. Dublin Soc.*, giving tables similar to Hartley's, but indicating the order in which the lines disappeared on dilution by Greek letters (Table II, § 29).

The whole of their work was done with the first medium quartz spectrograph of fixed adjustment type. I designed this instrument for Hartley about 1909, and in its optical dimensions and general principle it is closely followed by the medium quartz spectrographs of the present day.

§ 112. The Sensitive and Ultimate Lines in the Spark Spectra of Solids (de Gramont, 1907).—This investigator was led by his spectrographic work on minerals to determine which radiations of the various elements were the last to disappear as the amount of the element present was diminished, the spectra being produced by a condensed spark discharge from a substance, solid, liquid, or in fusion. Those radiations which are still shown when an element is present in very feeble quantity he called *raies sensibles*, and those which remained last of all when the amount was decreased *raies ultimes*.

The definition of *raies ultimes* was first given by M. de Gramont in a note presented to l'Académie des Sciences in the course of the meeting of May 21st, 1907. The following observation appears at the end of this note (*translation*) :

" *Raies ultimes* or lines of great sensitivity are the same for the condensed spark, the spark with or without self-induction, the arc, and very hot flames. This statement appears to simplify investigations in spectrum analysis."

These rays were stated by de Gramont to present the following characteristics :

(1) They are not necessarily the strongest lines in the spark spectrum of the element.

(2) They still remain if in the condenser circuit is inserted a self-induction even of as much as 0·1 H.

(3) They belong also to the arc spectrum of the element, where they are generally of great intensity.

(4) They are generally present also in the spectra of very hot flames (oxy-hydrogen or oxy-acetylene).

De Gramont found these results to hold for alloys, minerals, and fused salts, and states that they are in general agreement with those obtained by Pollok and Leonard in the case of solutions, a fact which greatly increases the value of all the tables of these observers.

The order of sensitivity is that found by photography either with a quartz or with a " Uviol " crown spectrograph, and it is in the ultra-violet that the *raies ultimes* almost always lie. Where *raies sensibles* are recorded in the visible spectrum they are often of high sensitivity for the eye. This is notably the case with barium, cæsium, calcium, chromium, gallium, indium, iron, lead, rubidium, strontium, and zinc.

§ 113. The conclusions of de Gramont require modification. Negresco (1927*a*) showed that the incompatibility of various data for spectrochemical analysis is due to the different conditions, electrical and otherwise, employed by these investigators. The main conclusions of his researches may be summarized as follows :

(1) When the content of a metal in an alloy serving as the source of emission decreases, the intensity of all the lines of this metal decreases progressively and continuously until they disappear completely. This diminution occurs in the same way for all the lines due to the metal, whatever their nature or origin.

(2) The sensitivity of any spectral line in a given source depends solely on its intensity in the spectrum of the pure metal obtained under identical conditions. Thus the order of the lines classed by decreasing quantitative sensitivity is the same as if classed by decreasing intensity in the spectrum of the pure metal, both in the case of arc and of spark spectra.

(3) For spark spectra the classification is independent of the action of self-induction on the different lines. It does not depend upon the presence or absence of different lines in the flame spectra.

(4) The classification considered *above* is independent of the alloy containing the metal. The same metal may, however, be more sensitive to detection in one series of alloys than in another.

(5) The most sensitive lines are always present in the flame spectrum, and particularly in the envelope, where they are of remarkable intensity. The converse of this statement is not always true ; there are lines which appear with considerable intensity in the spectrum of the flame envelope which, however, are weak and relatively less sensitive in the arc and spark spectra.

It will be seen that these conclusions do not agree closely with those of de Gramont. Nevertheless, the work of de Gramont, like that of Hartley, Pollok and Leonard, has been of inestimable assistance to all subsequent workers in guiding them to where in the spectrum to look for the lines likely to be present when only very small quantities of a metal are contained in a substance. A complete list of the papers of these workers and of their tables is given by Twyman and Smith (1931).

Reference on the subject of *raies ultimes* should also be made to §§ 30 and 39.

De Gramont's work appears in a long series of papers from June, 1899, to February, 1922. An account of his work during the war of 1914-1918 was published in 1920.

§ 114. Regular Use of the Spectroscope for Inorganic Analysis.—Sir Herbert Jackson was to my knowledge regularly using the spectroscope well before 1908—and I think even before 1898—for qualitative analysis. He considered that for precise inorganic analysis it was essential to test filtrates and precipitates (after weighing) for traces of metals which might be imperfectly separated or which might not have been looked for.

He also used spectroscopy for the examination of Chinese porcelain. The method he employed has already been described in Chapter V (§ 81).

§ 115. Quantitative Analysis by Synthetic Matching ; Pellet and Ratio Quantitative Methods (Lewis, 1916).—This paper by Judd Lewis, dealing with the regular application of spectrochemical analysis in his work as a consulting chemist, was far in advance of any other publication. It establishes him as the first to apply the method as a regular means of analysis in industrial problems. Judd Lewis started to use the spectrographic method in 1912, in studying the mineral constituents of certain tinctures and drugs.

His method was applicable to cases where it was easy to prepare synthetically a mixture containing the elements present in the substance to be analysed. A fundamental principle was that the material under analysis should be brought into the same physical and chemical condition as the synthetic mixture.

Later on Judd Lewis fully developed and used his pellet method (1936, p. 24). In this an ash or other powder was compressed into a pellet and placed on the lower pole of a copper or silver arc. By synthesizing a second pellet, whose composition was known, so that its spectrum exactly matched that of the one under analysis, he obtained the required quantitative analysis. The procedure is then as follows :

(*a*) Convert the material to be analysed into a sulphate or sulphated ash by any suitable method, completing the reaction by moistening with a very little dilute sulphuric acid and fuming this off by gentle heating. No more than a little free acid should remain. The product is then finely powdered with a precisely equal weight of spectroscopically pure ammonium sulphate. Ten-mg. portions of this mixture are then weighed out and pressed into pellets. One pellet is placed on the lower electrode of an arc lamp, and the arc is struck by drawing across the electrode gap a third electrode. It remains only to conduct the arcing under constant conditions. The conditions may vary considerably, but they must be maintained strictly constant throughout the series of experiments to be compared.

Whatever the electrodes selected, they should be of the highest purity ; copper electrodes are recommended for ordinary work.

The arc gap should be about 2 mm., and the voltage maintained at 32 to 33, control being effected by varying the gap slightly. Exposure : two minutes.

(*b*) From the resulting photograph make a qualitative analysis.

(*c*) Synthesize a sulphated ash so that its spectrum matches that of the sulphated specimen under test.

Still later Judd Lewis made use of a further principle, which he calls the " ratio quantitative method " ; by chemical determination of the main ingredient in the specimens to be analysed combined with spectrographic determination of the ratio of the minor ingredient to the main one, as, for example, in the ash of a plant, he is able to state at once the percentage of the minor ingredient in the original substance. Judd Lewis claims that an accuracy of 10 per cent. can be attained by these means, and no quantitative method of like accuracy requires less in the way of apparatus.

§ 116. Early Industrial Use of the Large Quartz Spectrograph (Bassett and Davis, 1923).—This paper was written after eight years' experience of the use of spectrochemical analysis in the laboratories of the American Brass Company, Waterbury, Connecticut The spectrograph was used for the determination of indium, gallium, and germanium in zinc ; for the detection of antimony in lake coppers, and the detection of bismuth in zinc and in other alloys ; and also for examining high-conductivity copper for arsenic, nickel, etc. Residual traces of boron, magnesium, silicon, and other de-oxidizing agents were successfully detected where wet analysis had failed.

No quantitative methods were used, and there is no technical information in the paper of much importance to-day, but the authors seem to have been the first to use the spectrograph regularly in the laboratory of an important metallurgical works The instrument was in 1939 still in regular use in the laboratory of the company, having seen twenty-six years' continuous service.

§ 117. The Internal-standard Method, and Homologous Line Pairs (Gerlach, 1925 ; Gerlach and Schweitzer, 1931a).—In this paper Gerlach describes the "internal-standard method," of which a good account is given by D. M. Smith (1933) :

"The intensities of the impurity lines are compared with those of neighbouring lines due to the predominant metal in the alloy. This obviates any difficulties arising from small variations in the intensity of the spectrum as a whole (and hence the intensities of the impurity lines) which may arise from fluctuations in the light source, development of the plate, etc.

"Care should be exercised in the choice of lines as intensity standards. For example, the copper 'spark' lines appearing in the arc spectra of copper samples (see p. 17 [list of such lines]) are quite unsuitable if one is working with a spherical condensing lens, and unsatisfactory even when a spherocylindrical condenser is used, on account of the unavoidable wandering of the arc discharge round the poles of the electrodes. Moreover, it is difficult to compare sharp and diffuse lines with exactitude and results obtained in such a case may not be comparable unless exactly the same slit width is used for all analyses. . . ."

The internal-standard principle is now universally recognized by all using spectrochemical analysis. Not long since I came across a provisional patent which I applied for in 1907 for an apparatus intended to utilize this very principle, and remembered that I had had an instrument made at that time embodying the principle. By an arrangement of double-image prisms spectrum lines of the main element and of the minor constituent were brought into juxtaposition, and the stronger was reduced by a polarization photometer till it equalled the weaker. I do not remember that anyone was interested, or that any publication took place. The instrument was born before its time, and was unnecessarily complicated ; simpler forms on the same principle are available to-day (*e.g.* that by Mandelstam, Smirnow and Zehden, 1936).

§ 118. In the use of internal standards, theory and observation alike support the recommendation of Gerlach and Schweitzer to use for the measurements wherever possible only lines whose intensities relative to each other do not vary with even widely varying conditions of the arc or spark ; in this method these authors confine themselves to the use of lines whose intensities remain equal to each other under widely different conditions of excitation, for, as Gerlach points out, such lines remain of equal intensity even when they are over- or under-exposed. Gerlach uses these " homologous line pairs," as he calls them, as the basis of his system of analysis. To do so is a severe restriction on the choice of lines, but, working with the microphotometer, one can use also line pairs of unequal intensity, though these should still be selected so that the ratio of their intensities does not alter with changes in the conditions of excitation.

As a means of ensuring that the electrical conditions of the spark are standardized Gerlach uses as a criterion lines of the main substance which alter greatly with changes in the electrical circuit. These he calls " fixation pairs " of lines (see also § 40).

§ 119. Use of Auxiliary Spectra (Schweitzer, 1927).—Lines to be used as internal standards must be close to the lines with which they are to be compared, and both lines must lie within a suitable range of blackening. The methods employing stepped spectra enable one to compare lines of widely different intensity, and Breckpot (1939) has given special attention to this.

Another way of dealing with the problem is by means of the auxiliary spectrum or *Hilfsspektrum.*

Smith (1933) describes Schweitzer's *substituierte Hilfsspektrum Methode :*

" . . . In cases where there are few suitable lines available as intensity standards in the neighbourhood of the impurity lines, the number of such standards may be artificially increased by the use of an auxiliary spectrum which is coupled with that of the sample under test. The auxiliary spectrum principle was first applied to the analysis of metals and alloys by Gerlach (1928).

" To obtain the lines in the auxiliary spectrum of a standard intensity relative to that of the sample, the times of exposure are varied until a selected pair of lines, one line in each spectrum, are of equal intensity. This equality of intensity standardizes the ‘coupling’ for subsequent work. . . .

“In practice, the two spectra are photographed either together or slightly overlapping (by suitable racking of the dark slide) in order that the lines in each spectrum may be easily recognized.

“A variation of this method, which is useful where only one or two lines due to the impurity are present, is to adjust the relative times of exposure until the lines in the auxiliary spectrum bear a definite intensity relationship to the impurity lines. In this case the auxiliary lines are compared with the internal standards in the spectrum of the sample under test and the analysis carried out in the same way as before. . . .

“The auxiliary spectrum principle is capable of considerable extension and suitable spectra can be chosen after a certain amount of preliminary experimental work. The nature of the impurities to be estimated and the position of their sensitive lines, the dispersion of the spectrograph and similar matters will give some indication of the most useful metal or alloy to be selected for this purpose.”

Another way of producing an auxiliary spectrum is that of Whalley (§ 214).

The internal-standard and auxiliary-spectrum (sometimes called the substitution) methods have been used extensively by Smith (1933), who gives valuable information concerning the assay of zinc, tin, lead, and copper.

Table VI shows the method of presenting the results.

TABLE VI.—RESULTS OBTAINED FOR CADMIUM BY THE SUBSTITUTION METHOD.

Cadmium, per cent.	Comparative Strength of Lines:				
	Cd 2265·0.	Cd 2288·0.		Cd 3466 2.*	
0·001			= Sn 2333		
0·005	bv† < Sn 2267·2	< Sn 2282·2	>	bv	
0·01	=	=			
0·05	>	>		< Sn 3223·6	
0·1	< Sn 2268·9			=	< Sn 3218·7 (0·2)
0·5	=			>	>

---

* Intensity comparisons with this line (and also with 3610·5 and 3403·7 A.) are difficult on account of the strengthening in the region corresponding to the negative electrode.

† bv = barely visible.

§ 120. The Twin Spark (Barratt, 1928).—This method has never received the attention it deserves, although the principle has been used by Triché (§ 141). It ensures that both the standard specimen and that under analysis are excited with identical energies.

The first claim of British Patent 320,136 reads :

> " 1. Apparatus constructed and adapted for effecting spectroscopic or spectrographic analysis on the principle of comparing the intensities of the spectrum lines of an element emitted from two separate equal sparks derived simultaneously from the same electrical source, one between poles of the material under examination and the other between poles of a standard preparation of the element."

The patent lapsed in May, 1937.

(The following description was prepared by Mr. S. Barratt, formerly of the Spectroscopic Department, University College, London, the inventor of the method.)

"The procedure depends upon the photometric comparison, visual or photographic, of one or more lines of the element when excited simultaneously in the " unknown " and in a standard comparison material under electrical conditions which are identical.

"In practice, the unknown and the standard are made into the poles of two spark gaps arranged electrically in series, so that fluctuations in the discharge must occur in each simultaneously. The two spark gaps can be arranged on a common mount, and their lengths are made equal. The photometric comparison of the spectra may be made in the visible region by using, for example, a Nutting photometer in conjunction with a constant-deviation spectroscope, or photographs may be taken and the intensities derived by microphotometer in the usual way.

"The principle can also be employed in the ultra-violet by using a sector photometer together with a quartz spectrograph, the sectors being adjusted to various apertures corresponding with the limiting percentages of the constituent which are permissible.

"The conditions for the most successful application of the method to each individual problem have still to be determined. The reproducibility of results within the observational error has, however, been established in my laboratory. Repeated measurements with two pairs of electrodes of the same material, for example, will always give the same relative intensities in their spectra."

Another application of Barratt's twin spark is also possible when a photometer is not available. The sparks are used as before, but in place of the single standard a series of standards of known composition are introduced successively, and the intensities compared with that from the unknown, either visually or photographically, the images being brought into juxtaposition on the spectroscope slit by a biprism or other suitable optical device. It seems that the method might be very useful where the composition of an alloy is to be kept within specified percentage limits.

§ 121. The Logarithmic Sector (Scheibe and Neuhäusser, 1928).—The application of this device to spectrochemical analysis is due to G. Scheibe and A. Neuhäusser, although it should be noted that in 1925 (three years before the first publication of Scheibe and Neuhäusser on the subject) Thorne Baker mentioned in a lecture before the Royal Society of Arts the use of a "Belin" sector (*viz.* a stepped logarithmic sector) in front of the slit of the spectrograph as a means of quantitative spectrochemical analysis. It is a disc whose periphery is cut to a logarithmic curve, and which is rotated in front of the slit, so that the exposure is made to vary along the slit (Fig. 38). This results in the lines on the spectrogram being of different lengths, which are thus a measure of their relative intensities, as shown in Fig. 39.

The logarithmic sector has been used by a number of workers in the last five years with both the arc and the spark. To give one example only, Slavin (1933) used it in determining cobalt, iron, copper, cadmium, thallium, germanium, and lead in concentrated zinc sulphate solutions, and iron, copper, cadmium, and lead in metallic zinc. His procedure is the same as that of Twyman and Hitchen (1931*b*)—§ 130—in that he uses salts packed into holes drilled in pure carbon electrodes instead of the solid metals; he achieves an accuracy within 10 per cent. for the majority of tests, with occasional errors amounting to 20 per cent. The speed permits the method to be used in the works control of such operations as involve the removal of metal below an arbitrary concentration. Slavin uses the dried salts, since it is then easy to make mixtures of known composition for producing working graphs.

It appears that an accuracy of within 10 per cent. in determining a minor constituent is usually obtained by the use of the logarithmic sector. The method is simple, but it is very difficult to define precisely the end-points of the lines. Foster and Horton (1937) find this difficulty reduced by the use of a special optical comparator, whereby the two lines are brought adjacent to one another and moved until they taper off together. These authors also replace the sector by a graduated wedge film of aluminium.

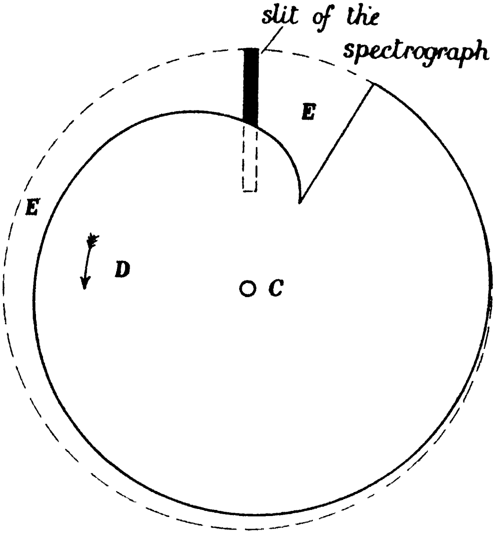
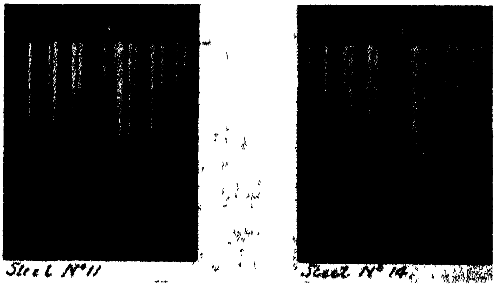


Fig. 38.—Logarithmic Sector.



1·01 % Cr. 0·23 % Cr.

Fig. 39.—Spectrograms obtained with the Logarithmic Sector.

It is partly this difficulty of defining the end-points of the lines which favoured the use of the stepped sector, in which the periphery is cut into such steps that each spectrum line gives in effect a number of exposures in geometrical progression. The stepped sector can be used in conjunction with the microphotometer (§§ 136-138).

§ 122. Twyman and Simeon (1930) considered the factors concerned in getting accurate readings with the logarithmic sector. They are worth quoting, as some of them are applicable to methods of stepped spectra :

" In using the wedge sector for measurements of the intensity of spectrum lines it is necessary to secure that the variations of blackening of the photographic plate along the lines of the spectrum are entirely due to the sector. Other factors may produce such variations if not guarded against, and these must be avoided.

" (1) The jaws of the slit must be parallel. This becomes of importance where a smaller slit width is used than corresponds with the diffraction image of the line. Since, under favourable conditions, an accuracy of intensity measurement of 2 per cent. can be reached by the wedge method, it will be seen that the accuracy of slit width desirable is very great, if the finest slit is to be used. Where the spectrum is not too complex, wide slits may with advantage be used. Such wider slits reduce also errors arising from causes mentioned in (2) and (3).

" (2) For a like reason the slit must be clean.

" (3) The definition of each spectrum line must be uniform along its length, or, if this condition is not fulfilled, only so much of the length must, for best results, be utilized as is uniform.

" (4) Variable magnification (" distortion ") along the spectral images of the slit is a conceivable source of error, but can be ignored in all ordinary spectrographic apparatus.

" (5) The sector should be placed as near the slit as possible.

" (6) The spectrum lines must each be illuminated by a like area of the light-source. This condition can be fulfilled by an image of the light-source being formed by a spherical condensing lens not, as is customary, upon the slit, but upon the prism of the spectrograph. The position and size of the light-source and the focal length and position of the condenser must be such that the image of the light-source must lie wholly within the effective aperture of the spectrograph—usually limited by the prism. This is another reason why a wide slit should be used where possible —otherwise, owing to diffraction, the condition referred to in this paragraph may be difficult to fulfil.

" The attainment of this condition is best assured by observation from the camera end of the spectrograph. The eye placed in the region of the visible spectrum can see the image of the light-source, and the observer can thus assure himself that the image is not obstructed. A margin must be left sufficient to ensure that the condition is fulfilled not only for the visible, but for the ultra-violet part of the spectrum, and also to provide for possible wandering of the light-source.

" Other points requiring note are :

" (7) Owing to the chromatic variations of focal length of the lenses of quartz spectrographs, the spectrum lines are of varying length, and never of the same length as the slit except at one point of the spectrum. The lengths of the " wedge " lines measured on the spectrum must therefore be corrected before any precise inference can be drawn from them concerning the variation of intensity indicated by variations in length. If observations on the standard alloys are made on the same instrument, this condition can obviously be ignored.

" (8) The spectrograph must be " stigmatic," that is, a point of the slit must be represented on the photographic plate by a point image. Thus a grating spectrograph is not usually suitable unless it be of the stigmatic type.

" (9) The speed of the sector must be such that during the shortest exposures the sector must make at least 40 or 50 revolutions. . . . The reason for this condition is that part of the line receives light for a number of intermittent exposures which may be materially (a large fraction of unity) different from that operative for another part of the line.

" (10) The development of the plate must be uniform. When in applying this sector to quantitative spectrum analysis by the method of Scheibe and Neuhäusser lines near to each other can be compared, little care is needed to secure sufficiently uniform development, for modern commercial plates can then be relied on to be sufficiently uniform over a sufficient area for no errors to arise from this cause.

" (11) It is desirable that the plates and mode of development used for the standard range of alloys of known composition should be the same as those used in actual determinations.

" (12) The substance under examination must be of uniform composition (as are most metallic alloys, solutions, and possibly powders thoroughly ground, mixed and carefully sampled)."

§ 123. The logarithmic sector has been used also by Fagiolo (1936), Martin, Burke and Knowles (1935), Burke (1937), Schubert and Cruse (1935), Kaisin (1937), Slavin (1933), Twyman and Fitch (1930), Twyman and Harvey (1932), Twyman and Hitchen (1931*a*), and Smith (1933).

The work of Twyman and Fitch was concerned with the analysis of steels. Twenty different steels were specified and obtained by Professor C. H. Desch, of the Metallurgical Department, Sheffield University, the chemical analyses of the whole of which were conducted at Sheffield University under his direction by Dr. F. Ibbotson and Mr. E. Gregory. The steels were manufactured by Messrs. Kayser Ellison & Co., Ltd., of Sheffield, and were specially rolled by them to the required size.

The work of Twyman and Harvey was conducted on the same specimens, and dealt with the estimation of nickel, manganese, and chromium by the same method in the light of an examination of the results of Twyman and Fitch. Twyman and Harvey found that the line intensity as determined by the logarithmic sector when plotted against the percentage of the constituents present gave as graph a straight line over considerable ranges, and that, even when the limits of that range were exceeded, a linear relation was usually found if the logarithm of the intensity was plotted against the logarithm of the percentage.

The investigations of Twyman and Hitchen were concerned with the estimation of metals in solutions by means of their spark spectra. In this paper the effect was described of the variation in the intensity of the line of one constituent when another constituent was present. This effect is now well recognized, and is not explained by the reduction in the percentage of the main metal.

§ 124. Spectrochemical Determinations by Measurement of Line Lengths (Occhialini, 1929).—A. Occhialini (at the University of Genoa, Italy) investigated a method of quantitative spectroscopic analysis based on the measurement of the lengths of the lines of the element sought in the spark spectrum of the substance. The method was suggested by Lockyer (§ 28.1).

The method is primarily a visual one. The image of a *horizontal* spark is focussed on the vertical slit of the spectroscope with a lens mounted so that it is capable of lateral movement by means of a micrometer screw. One watches the spectrum while moving the image of the spark across the slit of the spectroscope by means of the micrometer. The distance one has to move from where the selected line first appears at the electrode to where it just fades away to zero is dependent on the amount of resistance inserted in the discharge circuit. A characteristic curve for the line is obtained by plotting the lengths of the lines against the values of the resistance, and from these the author deduces curves giving the relation between the lengths of the lines and the concentrations of the element sought.

This method is applicable to both low and high concentrations. For high concentrations less capacity is used than for small concentrations, in order to obtain lines of suitable length for measurement. The complete curve for a single concentration requires half an hour for its investigation.

It was intended to carry out experiments to determine whether the ratio of the lengths of two lines due to different constituents of an alloy or solution depends only on the relative concentrations of these constituents, and not on the conditions of the discharge. If this should be the case, this ratio would form the basis for absolute determinations of the constituents.

The following observations, which are of more theoretical interest, were made by Occhialini :

(1) All the lines of the same order of ionization of an element are related to a single curve.

(2) The ratio of the lengths of the components of doublets and triplets of the same series is constant.

(3) The length of an arc line is not influenced by the polarity of the electrode.

(4) The length of a spark line (*e.g.* Mg 4481) is greater when the electrode is positive than when it is negative.

(The last two results are evidence of the fact that the atoms which emit the arc lines are neutral, while those which emit the spark lines are positively charged.)

The method has been used by Pastore (1937) in the determination of carbon, chromium, nickel, sulphur, silicon, phosphorus, titanium, manganese, molybdenum, tungsten, and vanadium in steel. It must be noted that Occhialini's method includes the observation of the cathode layer (§ 85), and is therefore very sensitive. Pastore actually determined carbon from 0·02 to 0·3 per cent. ; phosphorus from 0·0007 to 0·012 per cent. ; and sulphur from 0·0005 to 0·01 per cent.

§ 125. Liquids dried in a Hollow Graphite Rod (Nitchie, 1929).— Following Loewe (1928) Nitchie put the solution in a hollow graphite electrode, which was dried in an oven, and used as one electrode of an arc.

Braidech and Emery (1935) have used a similar procedure in the analysis of water supplies for aluminium, barium, boron, copper, chromium, fluorine, lead, nickel, manganese, potassium, sodium, silver, strontium, and zinc. Preparation of the substance consists in evaporation to dryness of 2-litre samples of the water ; a few milligrams of the residue are arced in a small cavity in a pure electrode. The quantitative method was apparently the internal-standard method, but the paper does not make this too clear. The investigation was concerned in the first place with the possibility of injurious mineral impurities in water supplies arising from coagulating the water by the use of aluminium sulphate in syrup form ; it was extended to a survey of various typical water supplies in the United States. Lists of the waters and analyses are given.

In a tentative method of test published by the American Society for Testing Materials (1937), high-grade pig-lead is examined for copper, bismuth, silver, nickel, antimony, tin, and cadmium. Excitation : graphite arc. Preparation of substance : weighed turnings or filings are dissolved in nitric acid, the solution being introduced into a hole in the graphite electrode and spectrographed. Quantitative method : comparison with spectrograms of standard solutions.

§ 126. The Microphotometer (Chapter IV).—This gives an accuracy distinctly greater than that of the logarithmic sector, and by using the microphotometers of the non-recording type which have been designed for this kind of work, routine analyses can be carried out very quickly. Among the users of this method are Lundegårdh (solutions and acetylene flame—1929 and 1934), Findeisen (lead alloys—1933), Duffendack *et al.* (solutions used with the spark—1933), Breckpot (general analyses using the stepped sector—1937), Whalley (aluminium alloys with the spark—1937), and most of those using the spectrograph for metallurgical analysis to-day (see Chapter IX).

In confirmation of the superiority of the microphotometer to the methods of wedge or stepped spectra (logarithmic sector, etc.) one may instance the work of Cholak (1935) on the quantitative spectrographic determination of lead in biological material. In his earlier work, he used a rotating logarithmic sector ; later he preferred microphotometer measurements.

§ 127. An instrument with which measurements of blackening of the plate can be made ten times as accurately as by eye could not long escape the notice of spectrographers, and seven years ago it was already being applied by them. Some of the claims to very high accuracy then made were scarcely justified, for some of the authors had neglected to make use of the experience of the physicists; but in 1933, Duffendack was (in exceptionally favourable cases) achieving an accuracy approaching 1 per cent. in the analysis of solutions (§ 137).

The astrophysicists, who used the microphotometer for measuring the intensities of stellar spectral lines, found it necessary to calibrate each spectrum plate by imposing upon it a set of exposures of differing but known relative intensities, thus producing stepped spectra. This was the principle adopted by Duffendack.

The procedure preferred in my laboratory for practical analysis is described in §§ 64 to 69.

§ 128. Direct Photometry of the Lines.—A few workers have used direct photo-electric comparison of the intensities of the lines without the intermediate step of taking a photograph, and doubtless where one kind of determination has to be made very frequently such an arrangement may be quick and accurate. There are few laboratories, however, where so specialized a method is worth while—but see Lundegårdh (1929) and Jansen, Heyes and Richter (1934).

§ 129. Analysis from Graphs obtained with Known Samples (Lomakin, 1930).—In this paper Lomakin describes the method which is most in vogue to-day for the analysis of metals and alloys. He calibrates the plate on which the spectra of the alloys are photographed by adding spectra of standard alloys, the compositions of which have been carefully determined by chemical means. Measurements are made by the microphotometer. The method as carried out in my laboratory is described in §§ 64 to 69.

§ 130. Powders in a Hollowed Graphite Electrode, using the Logarithmic Sector (Twyman and Hitchen, 1931b, p. 22).—An arc method was devised by Twyman and Hitchen whereby representative spectrograms can be secured from powders, etc. without special preliminary treatment of the material. After very careful sampling, 1 to 3 g. of the powder is taken and packed into a hollowed-out graphite electrode. The exposure (employing the logarithmic sector) must be fairly lengthy in order to ensure that all of the powder is consumed, and is generally of the order of 5 to 20 minutes (thus permitting a certain control of sensitivity). It should be noted that—in order to avoid over-exposure—it is necessary to place the arc at a greater distance from the slit than is generally used. The method is simple and rapid, and appears to be applicable to a very wide range of substances.

§ 131. **Nitchie and Standen** (**1932**) describe an extension of the auxiliary-spectrum method of Gerlach and Schweitzer (§ 119). They bring the substance into solution and introduce into the solution in known amount an element not originally therein, to furnish spectrum lines which serve as comparison standards. They give, as an example, the determination of magnesium in a zinc-base alloy. A measured quantity of the solution of the sample is introduced into a hole in a controlled graphite electrode, which is placed in an oven and dried for 45 minutes at 110° C.

A rotating sector wheel with a 10 per cent. opening is used to cut down the amount of light to a suitable intensity for photometry, while yet permitting the arc to burn for a sufficient length of time for complete utilization of the whole of the residue under test. (Bauer, 1940, also brings the metal into solution.)

§132. Slavin (1933).—Slavin's method for powders has already been mentioned (§ 121). The specimen is introduced in powder form into a hollowed carbon electrode, which is used to form an arc, and a logarithmic sector is used.

§ 133. Milbourn (**1937**) used a hollowed graphite (or sometimes copper) electrode for examining soils and plant materials. To keep the method as simple as possible the material was tested as a dry powder, the only preliminary treatment being careful sampling and grinding so that the sample taken for analysis was representative of the bulk. A very short arc (only 1 mm.) was used, as it was found to reveal smaller quantities of the elements.

§ 134. Sensitive Methods (Späth, 1932).—Späth is concerned with sensitiveness, expressed not in percentages but in actual quantities. He states that the smallest quantities hitherto observed have been determined by means of the spark, that in this way 10^{-10} g. of lead, 10^{-10} g. of manganese, 10^{-8} g. of zinc, and so forth have been determined by previous workers, and that in comparisons which have been made by them it has been found that the interrupted arc is more sensitive than the spark. The purpose of Späth's paper is to make a comparison between the spark and the interrupted arc.

No stress is laid on any special instrumental method, the paper dealing chiefly with the purification of the electrodes which formed the foundation of the substances examined. The amounts of various metals detected are indicated in Table VII.

TABLE VII.—SENSITIVITY OF SPARK AND INTERRUPTED ARC.

Element.	Smallest amount detected in the	
	Spark, g.	Interrupted Arc, g.
Cadmium . . .	10^{-10}	10^{-10}
Manganese . .	10^{-10}	10^{-8}
Thallium . . .	10^{-8}	10^{-9}
Iron . . .	10^{-7}	10^{-9}
Arsenic . . .	10^{-7}	...
Lithium . . .	10^{-9}	...
Strontium . .	10^{-11}	...

Späth says that the most important of the factors which limit the spectrochemical detection is the background, *i.e.* the general blackening which appears with long exposures, and which makes the detection of weak lines extraordinarily difficult. Concerning the origin of this background see Gerlach and Schweitzer (1930, p. 15) and §§ 67 and 72.

It is naturally to be expected that with a spectral apparatus of great dispersion the effect of the background would be diminished. The above figures, therefore, do not indicate the extreme sensitiveness that could be obtained with suitable apparatus. (The apparatus used by Späth was a quartz spectrograph giving a dispersion from 6000 to 2100 A. of 9·3 cm.)

§ 135. Publications concerning the Use of the Feussner Spark.—The Feussner interrupted spark has already been described in Chapter V (§ 87. 1, *b*). The experience of some of the users will be found in the following papers :

Lay and Keil (1937) describe in a short paper the works control of magnesium and other metals in light alloys. 12,000 tests were made in one year. The authors mention the lines used, the accuracy attained, the mode of preparing the specimens, and other useful details.

H. Kaiser (1936-7) gives a clear statement of conditions which he considers must be fulfilled to secure accuracy in quantitative analysis, with particular reference to lead alloys and light alloys. The author shows what excellent results can be obtained under carefully controlled conditions.

Scheibe and Schöntag (1934) refer to the causes which others have supposed to produce the errors which the latter found in the spectrochemical determination of silicon in iron and steel. They consider it necessary to investigate the matter lest the impression gains ground that a very expensive sparking apparatus is necessary for this kind of work. A very thorough investigation was made of the effect of the various sources of error, and the authors state the mean accuracy which they find obtainable with their technique (using a simple condensed spark with self-induction and resistance in the high-tension circuit, microphotometer and the lines Si 2516 and Fe 2518) to be from ± 3 per cent. for silicon in steel up to ± 11 per cent. for silicon in grey cast iron, containing from 0·2 to 1 per cent. of silicon.

Seith and Beerwald (1937) used the interrupted spark in the analysis of magnesium and aluminium alloys. The work was undertaken with the object of investigating the diffusion of magnesium into aluminium, but the results on diffusion are promised to appear in a later communication. The paper deals with the quantitative analysis of the various phases of magnesium-aluminium alloys.

Kosbahn (1936) investigates the properties of (*a*) the "single spark" (*i.e.* as in the Feussner apparatus—§ 87. 1, *b*) using an apparatus similar to that of Sawyer and Becker (1923)—§ 87. 1, *a*, and (*b*) the A.C. interrupted arc. The paper is an important one for those wishing to study the electrical theory of these types of spark.

Bauer (1940) was unable to obtain with solid electrodes an exact quantitative determination of manganese and magnesium in aluminium alloys—"exact" implying within ± 5 per cent. of the constituent. He attributed this to heterogeneity, and adopted the following procedure :

(*a*) Dissolve the specimen in the form of chips in hydrobromic acid, boiling off the bromine.

(*b*) Dissolve the resulting syrup in water.

(*c*) Bring a measured quantity of the solution on to a pure carbon electrode which has been previously heated by presparking.

The solution is absorbed by the carbon, which is then used for sparking.

Bauer used a Feussner sparking apparatus, but short-circuited the interrupter, so that the apparatus worked as a simple oscillating spark (see also Frommer, etc., § 165).

Stepped-spectrum Methods.

§ 136. We shall here group together some of the ways of applying stepped spectra. The principle of determining the relative intensity of spectrum lines by calibrating the photographic plate with stepped spectra has been fully described in Chapter IV (§§ 61, 62, and 63). Among the principal exponents of this application are Duffendack, with his collaborators, including J. S. Owens, who used the method in the laboratories of the Dow Chemical Company (Owens, 1938), and Breckpot. The particular methods of application adopted by these workers will now be described.

§ 137. Use of a Stepped Slit and Auxiliary Light-source for calibrating the Plate (Duffendack, 1932).—A description of this method occurs in a patent specification taken out in the name of the A.C. Spark Plug Company of Flint, Mich., U.S.A., of which the corresponding British Patent No. 418,298 has the following as its first claim :

" In the preparation of alloys having a predetermined proportion of a desired element, ascertaining from time to time the proportion of the element by producing on one and the same photographic plate a spectrogram of the alloy and a photographic standard of intensity of light, measuring the opacities of the standard and of a pair of selected lines of the spectrogram, determining the ratio of intensities of the selected spectral lines by comparison of the said opacities, evaluating the ratio in terms of the proportion of the element in the tested alloy by comparison with data of like tests of similar specimens of known composition and making such correction in the amount of the element in the alloy as indicated by the test as is necessary to attain the predetermined proportion."

The method as it appears in this claim seems to be clearly described in the passage from Dobson, Griffith and Harrison quoted in Chapter IV (§ 60).

I had an opportunity in 1933 of spending some hours with Dr. Duffendack at the University of Michigan, and was very greatly impressed with the accuracy of the method, as shown by the notebooks of readings which he kindly showed me. Measurements of the opacities of the lines were made, of course, by microphotometer. He was at that time employing the method in collaboration with Wiley and Owens, making analyses of urine for sodium, potassium, cadmium, and magnesium, and one of the matters engaging their attention was the effect on the intensities of the lines of one element due to variation in the percentage of another. Since the range of percentages covered was considerable, a good many graphs were required, but this difficulty had nothing whatever to do with the accuracy or convenience of the method as applied to routine analyses of substances in which the percentages of the constituents were either small or restricted to within a small percentage range.

It appeared to me by Dr. Duffendack's records that he was obtaining a consistency in the determination of the metals mentioned (in the form of solutions) approaching 1 per cent., and I attribute this in part to the homogeneity of the substance and in part to the careful calibration of the photographic plate. It must be remembered that this method of calibrating the plate was worked out by physicists over a considerable number of years, and had already been closely studied, as is shown by the above-mentioned extract from Dobson, Griffith and Harrison's book published in 1926.

Duffendack and others have published descriptions of this method and its use as follows :

Stepped Slit and Hydrogen Tube (*Duffendack*, 1932).—A method for measuring the relative intensities of spectral lines is described in which a stepped slit is substituted for the ordinary slit of a spectrograph. A continuous source of light (a hydrogen lamp) then produces on the photographic plate a set of bands over which the intensity of the light varies as the widths of the openings in the stepped slit. Necessary precautions in the use of the method are noted. Results from this method are compared with those obtained by varying the distance of the source. Possible errors in measurements of relative intensities of spectral lines due to the Eberhard effect and to the use of an intermittent source are mentioned.

Tube for Sparking Liquids, and High-voltage A.C. Arc (*Duffendack and Thomson*, 1936).—This paper describes a tube which is an improvement on the tube by Twyman and Hitchen (1931*a*), in that, instead of one electrode being metallic, the spark is developed between two electrodes of the solution to be analysed. The spark is struck between two horizontal jets of quartz or Pyrex glass, through which the solution flows at a constant rate from reservoirs connected to them.

The authors find that for analyses where only a drop of solution is available, the most convenient mode of excitation is a high-voltage, low-current, A.C. arc between pure carbons upon which a drop of the solution to be tested has been evaporated. The arc is excited by A.C. current through a 3-kva. transformer, the secondary voltage being about 1100. The A.C. current is stabilized by a number of choke coils and a variable rheostat in the secondary circuit, and is run on 2 amp. At this low current the arc will not maintain itself on clean carbons, and runs practically entirely on the salt, ceasing when the salt is exhausted. In the determination of sodium and potassium in concentrations of 0·01 to 1·0 per cent. of the former and 0·05 to 1·0 per cent. of the latter, 97 analyses for sodium and 76 for potassium showed that in no case did the error exceed 10 per cent., and errors of less than 1 per cent. occurred with great frequency.

Curves for Rapid Analysis (*Owens and Hess*, 1935).—In this paper Owens and Hess describe very briefly the use of a form of analytical curve for rapidly determining percentages from the readings on the spectrograms, using Duffendack's method. In a later paper Owens (1938) describes the very rapid routine developed from this.

Duffendack, Wiley and Owens (1935) describe the work which I saw in progress in 1933 (*above*). Quantitative determinations were made by the method described by Duffendack, Wolfe and Smith (1933). In this last-named paper the authors describe quantitative analysis by the method of stepped spectra. The distinctive feature in these papers is the calibration of the spectrograms by impressing on them an intensity pattern derived by a stepped sector, a stepped platinum wedge, or a stepped slit. All the papers should be consulted by anyone interested, since none of them by itself forms a complete presentation of the method and its possibilities.

§ 138. Breckpot (1933 to 1939).—In a long series of papers Breckpot describes the development to a pitch of considerable efficiency of methods of analysis distinguished by two main features :

(*a*) The use of a stepped sector like that used by Hurter and Driffield (1893), Eder (1898), Mees (1904), and others for the sensitometry of photographic plates. He most frequently uses sectors whose angular apertures are in geometrical progression with common ratios of 1·585, 2·0, or 2·51, and the number of steps is sometimes as great as twenty.

The sector is placed immediately in front of the slit, so that each spectrum consists of a number of strips each corresponding to a number of intermittent exposures of varying duration.

One finds the two strips in which a line of the main metal and of the constituent metal are respectively equal in blackening, and from this, with the aid of a graphical device (logarithmic divider), the percentage of the constituent is determined with great speed. If it is not possible to find two strips for which this equality of blackening holds, a rigorous interpolation can be made by microphotometer. Breckpot claims that, within certain limits of wavelength, the results are practically independent of plate factors and development.

The clearest and most complete description of this part of his method appears in Breckpot (1939).

(*b*) The use of copper oxide as a base in metallurgical analysis. One of the reasons for this is to avoid heterogeneity of the material. An application, which illustrates the method, is described in Breckpot (1935*b*). The whole series of papers in the *Ann. Soc. Sci. Brux.* (from 1933 onwards) must be referred to for a full appreciation of the advantages of the method for certain types of analysis.

§ 139. Powders and Precipitates in Filter-paper burnt in the Oxy-Coalgas Flame (Ramage, 1933; Steward, 1939).—In this method material is dried on filter-paper, which is subsequently burnt in an oxy-coalgas flame (as described in Chapter V).

The methods adopted by Ramage, Roach, and Steward and Harrison have already been described in §§ 74 and 75.

Dr. Robert L. Mitchell, who has been using Lundegårdh's apparatus for several years for routine examination, has recently tried the method of Steward and Harrison [illegible] apparatus which was loaned to him for the purpose. The following note by Dr. Mitchell is published with his own and Dr. Steward's consent :

"The Steward and Harrison method gives spectrograms suitable for quantitative determination with most of the cations which can be determined by the Lundegårdh method, although the range of sensitivity may be different.

"There is more possibility of flame control than in the Lundegårdh apparatus in use at the Macaulay Institute, and optimum conditions can probably be worked out for any cation.

"As an example of the accuracy obtained, I found that for manganese the standard error of the mean of 4 replicates was ± 6·1 per cent., whilst that for duplicates by the Lundegårdh method was ± 4·5 per cent."

This is less than the accuracy obtained by Dr. Mitchell in his use of the Lundegårdh apparatus, but less also than that obtained by Steward and Harrison for rubidium.

Hence it appears possible that, if used under the conditions prescribed and with attention to such small points of technique as are likely to be discovered by experience, the Steward and

Harrison method with its simpler apparatus is comparable in accuracy with the Lundegårdh.

Both Dr. Mitchell and Dr. Steward have prepared memoranda on the friendly comparison which is referred to *above*, and I do not doubt that they will communicate their opinions of the respective methods to anyone intending to take up this work.

I may here mention, out of its chronological order, the work of Roach :

Plant Material rolled in Filter-paper and treated in Ammonium Chloride Vapour prior to burning (*Roach*, 1939).—Roach has reported a method developed by Majewsky in which plant material rolled in filter-paper was immersed in ammonium chloride vapour and carbonized before introduction into the flame. He records a thirtyfold increase in the calcium sensitivity as a result of this treatment, and attributes this to increase of volatility of the chloride over the carbonate. Full information on this point is as yet unpublished. It would be interesting to have data for the effect of ammonium-chloride treatment and carbonization on papers impregnated with solutions.

Much of the difficulty experienced with Ramage's method has been, however, that of introduction of the paper roll or spill into the flame in a reproducible manner, and several of the workers who have tried the method have rejected it for this reason. The mechanical feed of Steward and Harrison (1939) largely overcomes this difficulty (§ 75).

§ 140. Increasing the Sensitivity of the Arc by the Globule Method (Milbourn, 1934).—" The problem which gave rise to this work was the necessity for making spectrographic analyses on small samples of copper, weighing less than 0·5 g. The usual arc method using copper rods was impossible, and the spark method was unsuitable on account of lack of sensitiveness ; it was decided therefore to try a globule method of arcing such as has been described for tin and lead by Smith (1933), Brownsdon and van Someren (1931), and Hitchen (1933), and for copper by Hill and Luckey (1919). Breckpot (1933) has also described somewhat similar work, in which synthetic samples, consisting of copper oxide with small additions of other oxides, were tested in a graphite arc.

" Working on small samples of copper, van Someren made the interesting observation that increased sensitivity to a number of impurity elements occurred when they were examined by the globule method of arcing. The present paper deals with the technique and line intensity comparisons to be used when applying this method to the detection and estimation of minute quantities of impurities in copper.

" The method used is essentially the same as that described elsewhere. An arc 4 mm. long and carrying 5 amp. is passed between a pure copper electrode, made the positive electrode, and a small portion (0·2 to 0·5 g.) of the sample to be examined, supported in a shallow cup in the end of a graphite rod. The piece of sample used is pickled, washed and dried on filter-paper. The voltage across such an arc is generally about 40 v. and does not vary by more than ± 1 v. for any one sample.

" The copper spectrum obtained from a globule arc is radically different from that given by a solid-electrode arc. The spark lines appearing near the poles in the latter are practically suppressed in the former, and many lines absent from or appearing only faintly in the solid-electrode arc occur with considerable intensity in the globule arc. The factors, such as temperature and electrical conditions in the arc, which favour the appearance of these lines, also enhance the impurity lines. Many of the faint " background " lines are nearly absent from the globule arc ; this also assists in the observation of impurity lines. The yellow luminous cone surrounding the arc, as described by W. B. Nottingham (1929), is very pronounced with the globule method.

" The results of observations on sensitivity to impurities made under identical conditions of amperage and arc length for the two methods of testing copper are given in Table [VIII]. Impurity lines which cannot be detected in the solid-electrode arc appear with sufficient intensity to allow of comparison with copper lines in the globule arc. The sensitivity to iron and silver, however, is not greatly increased."

Table VIII.—Sensitivity to Impurities in Copper of Globule and Solid-electrode Arcs.

Element.	Percentage.	Sensitivity in Globule Arc.	Sensitivity in Solid-electrode Arc.
ismuth .	0·0002	Bi 3067·7 = Cu 3068·9	Not detected
rsenic .	0·001	As 2349·8 visible	Not detected
ead . .	0·0004	Pb 2833·1 = Cu 2845·0	Not detected
on . .	0·002	Fe 2483·3 < Cu 2479·8	Fe 2483·3 visible
ickel . .	0·0005	Ni 3134·1 = Cu 3135·2	Not detected
ilver . .	0·001	Ag 3382·9 < Cu 3375·7	Ag 3382·9 < Cu 3375·7
ntimony .	0·002	Sb 2598·1 > Cu 2570·7	Sb 2598·1 barely visible
in . .	0·0005	Sn 2354·8 = Cu 2363·3	Not detected

§ 141. Twin-spark and External-standard Methods (Triché, 1937).—This is an important publication.

(1) Numerous reasons are put forward why the intensity of radiation emitted by two electrodes does not depend alone on the concentration of a metal in an alloy, and it is concluded that it is difficult to determine that concentration by measuring the blackening of the photographed spectrum lines.

(2) Several new methods are put forward in each of which it is only necessary to observe the equality of two lines. In these methods the following devices are employed :

(*a*) Two electrodes, one known A_1 and one to be analysed X, are placed on either side of a thin metal plate which does not contain the metal to be determined, and a spectrogram is taken. This process is repeated, replacing A_1 with other electrodes of known content A_2, A_3, . . . If the lines of a given minor constituent in A_n match those in X, the percentage of that constituent is the same in A_n and X.

(*b*) This is a development of the internal-standard method, using solutions. In applying this method to the analysis of aluminium-magnesium alloys, a series of alloys of known magnesium content is taken. A given weight of each of these is dissolved, and a known quantity of chromium added, making up with water to a standard volume. The quantity of chromium is varied until the 2802 Mg line equals 2766 Cr in intensity. A curve is then plotted connecting the concentrations of magnesium and of chromium which fulfil this condition. This is the calibration curve.

(*c*) *External-standard Method.*—In this one takes an alloy containing a metal M which is to be determined, and sparks between this and a solution containing an auxiliary metal B having a line near a line of M. If one produces equality of intensity of these lines, one establishes a definite relation between the concentration of these metals B and M.

(3) A large number of applications of local analyses of alloys using the high-frequency spark is given.

(*d*) *The Twin Spark.*—This paper describes apparatus for his twin spark and sector method—an attractive modification of the Barratt twin spark and sector (§ 120).

§ 141.1. Quantitative Analysis by Measurement of Width of Line (Eisenlohr and Alexy, 1937).—The excitation energy of an atom or ion which causes the emission of light of a particular wavelength can suffer secondary changes, which manifest themselves as strongly marked changes of frequency. "Collisions of the second kind" must lead to the same effect; collisions, that is, in which one atom does not communicate its entire excitation energy to a second atom, but retains a lesser amount σ in the form of heat. Ultimately, both phenomena lead to a broadening of the spectral lines which correspond with the original excitation energy. If, for example, a metal M is embedded in a ground substance, and both substances are mutually affected by interaction of the atoms, one would expect that an increasing proportion of the metal M would increase proportionately the width of the spectral line. The authors enquire whether this phenomenon of line-broadening can serve as a method of quantitative spectrochemical analysis; give a definition of "breadth of line" suitable for microphotometric measurement; and apply the method to the particular case of barium and strontium in pearl ash. They claim that in this kind of analysis the method has several advantages.

§ 142. Total-energy Method (Slavin, 1938).– Slavin in this paper points out that elements present in an arc or spark do not emit their spectra simultaneously, or at constant intensity. Goldschmidt and Peters have shown this very clearly by placing in a carbon arc a partly cupelled lead bead containing other metals and photographing the spectrum at intervals during the 170 seconds required for complete vaporization, the spectra of the various metals appearing (and disappearing) in the order: lead, silver, gold, palladium, rhenium, rhodium, platinum, iridium, osmium. The author, therefore, proposes as a suitable basis of quantitative analysis (in appropriate cases, *e.g.* minerals, ashes, and the like) *the total energy of the emission until all the specimen has been burnt off in a carbon arc.* The energy must be integrated by the photographic plate, and consideration is given to this problem. The author states that the procedure permits working over the entire range of concentration of the element to be detected from 0 up to 100 per cent. Although the principle of this method is implicit in Ramage's method, and although the procedure is closely similar to that of Twyman and Hitchen (1931*b*, p. 22)—§ 130, the author appears to be the first clearly to put forward this "total-energy" method in contradistinction to the measurement of intensities of the lines during *part* of the time that the substance is radiating.

§ 142. 1. Slavin (1940).—Developing this total-energy method (1938), in which Slavin finds that the spectral energy emitted by an element when it is vaporized in a carbon arc is directly proportional to the weight of the element consumed, he utilizes this observation as a basis for quantitative analysis. In the earlier paper he uses a quartz mercury arc lamp as an external standard of comparison. In the paper now cited he states that this mercury lamp left much to be desired when used for routine and analytical work. He says:

" It is appropriate to list the properties that a source intended as an external standard for spectrochemical analysis should have.

" Primarily, of course, it should be capable of reproduction, and the degree of reproducibility should be greater than the over-all precision of the whole process. On this basis, the allowable error for present-day practice should be of the order of 2 or 3 per cent. In addition, there should be no slow deterioration with age, a fault of incandescent lamps and of some enclosed metallic arcs.

" Radiation should consist of a line spectrum rather than a continuous one, because intensity of spectrum as photographed is a function of slit width, and this function is not the same for both kinds of radiation. The type of radiation should be the same for standard and analytical spectra ; otherwise slit width would have to be standardized, a matter of some difficulty and an additional complicating factor.

" The source should operate on direct current, as emission from an alternating-current source fluctuates periodically and thus cannot be used in conjunction with the usual photometric rotating discs (step, adjustable, and wedge sectors) because of the uncontrollable stroboscopic effects. The spectrum should be rich in lines, distributed over as broad a wavelength range as possible. Finally, the device should be simple to set up ; it should be inexpensive, and should require a minimum of change in the equipment of the arc stands and optical bench, so that the change-over from standard to analytical source may be accomplished quickly and easily.

" The source that fitted these requirements most closely was the iron arc, the only question—a crucial one—being on the score of reproducibility. In spite of the wide use of the iron arc in spectroscopy, there appears to have been no recorded work on this property. In his original description of the well-known arc form that bears his name, Pfund [1908] mentioned that when the anode was in the shape of a globular bead of metal, a very steady arc was obtained ; but he made no quantitative study of emission characteristics. Accordingly, this was the starting point, and the final form of the arc as discussed here is essentially similar to Pfund's."

The arrangement which the author found best is thus described :

* " The upper electrode, which is the negative, is a 0·125-inch graphite rod. The lower electrode is a spherical metal bead formed by feeding iron wire or cuttings into the burning arc. This bead is supported in a shallow cavity (formed by an ordinary twist-drill) in the end of a 0·3125-inch graphite rod.

" It is important that the iron forming the bead be pure to obviate fluctuations in emission due to differential volatilization effects. The iron wire used for standardizing volumetric solutions is an acceptable and convenient material. Before use, the bead must be ' seasoned '—that is, it must be burned in the arc until all spitting of molten metal has stopped. This violent action is probably due to oxidation of carbon and other gas-forming impurities in the iron, because when a gently burning arc is finally obtained, a matter of 3 minutes or so, the bead no longer has the appearance of metallic iron. As the necessary facilities were at hand, an X-ray diffraction pattern was made of one of these beads ; the results showed that it is a mixture of Fe_2O_3 and Fe_3O_4, principally the latter.

" The electrical circuit is identical with that of the ordinary low-voltage analytical arc, consisting of a variable series resistance in a 220-volt direct-current line. An ammeter is inserted in the circuit and is the sole control instrument. Electrode spacing is controlled by projecting an image of the arc on a neighbouring wall carrying marks to indicate the spacing. Once the resistance is adjusted, no other control is necessary but to feed the upper electrode down at the same rate at which it is consumed, and this is most easily done by feeding at a rate that keeps the ammeter needle at the predetermined point on the scale.

" The various emission studies were carried out by means of photographic photometry. A step-sector spectrum of the iron arc was included on each plate, the step-densities of a chosen line (Fe 3017·63) were measured, and a characteristic curve was plotted. Relative intensities were then determined by interpolating the measured density of the unknown line in this curve. The process is described fully elsewhere [Forsythe, 1937]. In the graphs the intensity values, where necessary, have been recalculated in terms of a standard exposure = 100, in order that all the graphs may be readily comparable. For this standard exposure the time was 1 minute, the current 4 ampères, and the arc gap 6·5 mm.

" The current range at which the arc will operate smoothly is limited. The relation between intensity and current is shown. . . . The lowest point, at about 2·3 ampères, represents the least value of current at which the arc will maintain itself. In the range represented by the linear portion of the curve, the arc burns very steadily with a hardly audible hissing sound, a slight, rapid wavering of the ammeter needle of about 0·03 ampère about the median value, and very little wandering of the anode spot on the surface of the molten bead. The cathode spot shows no tendency to wander. This is the current range at which constant emission is obtainable. Beyond about 6 ampères, where the break in the linearity of the curve occurs, the arc becomes irregular, the hissing sound becomes louder, and the cathode spot begins to wander, sometimes striking to the graphite support. The ammeter needle reflects this irregularity by rapid, wide fluctuations, thus making it very difficult to maintain the current at any fixed value.

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* If the reader needs to refer to the figure it will be found in the reference.

"*Applications of Iron Arc.*—Besides the use to which the standard iron arc is put in this laboratory, it should prove highly suitable for plate calibration in conjunction with the usual internal-standard procedure of spectrochemical analysis, particularly when one is forced to make multiple exposures, as with astigmatic spectrographs. A further possible use is in absorption work, where two separate exposures, one through the solvent and one through the solution, can be taken in place of the single exposure with a split beam. Hence, it would obviate use of a cumbersome piece of apparatus. Still another use is in miscellaneous test work in the laboratory, such as the determination of relative spectral sensitivity of plates, relative efficiency of condensing systems, and selective absorption of screens and neutral filters."

§ 142. 2. Metallic Impurities in Organic Chemicals (Hess, Owens and Reinhardt, 1939).—In determining small traces of metallic impurities in organic chemicals, these investigators remove the organic matter by wet ashing in spectroscopically pure nitric, sulphuric, and perchloric acids, a procedure very similar to that of Judd Lewis (§ 115). The resulting solution is evaporated nearly to dryness, and the residue is taken up in a definite volume of a solution containing the spectroscopic buffer and the internal-control elements. The spectroscopic buffer is an added amount of a suitable salt which eliminates the effects upon the analysis of the extraneous composition of the samples, and which permits the use of the same analytical curves (§ 137) for the analysis of samples which vary considerably in composition.

A 0·4-g. sample of the test material is weighed out on a watch-glass and transferred to a 150 mm. × 20 mm. Pyrex test-tube or a 30-ml. Kjeldahl flask. After the addition of 1 ml. of concentrated sulphuric acid the test-tube or flask is placed on a sand-bath heated by gas-burners. The sample is heated until charring is complete, after which concentrated nitric acid is added to aid in completing the oxidation. The nitric acid is added to the hot mixture a few tenths of a millilitre at a time until the solution becomes water-clear, denoting complete oxidation. In case the sample is particularly difficult to oxidize, a few tenths of a millilitre of concentrated perchloric acid is added to the sulphuric-nitric acid mixture after most of the free carbon has been destroyed.

When the solution becomes water-clear, it is evaporated to dryness to remove all sulphuric acid. The tube is cooled, and 1 ml. of concentrated nitric acid added. This solution is evaporated almost to dryness. Overheating must be avoided at this point, since some of the nitrates decompose rather readily, forming salts of low solubility. Excess heat may also change the form of some salts in such a manner as to affect the relative intensities of the spectral lines used in the analysis.

The residue is taken up in 0·4 ml. of a 2N. nitric acid solution containing the spectroscopic buffer and the internal-control elements, bismuth and molybdenum.

The arc electrodes are prepared as follows: Pure graphite rods 0·635 cm. (0·25 in.) in diameter are cut into 1·25-cm. (0·5-in.) lengths. The edges of one end of each section are slightly bevelled, and the end is polished on a clean paper towel. One drop of redistilled kerosene is added to the polished end of each section and allowed to evaporate. Each of a pair of the sections is then loaded with 0·03 ml. of the test solution. The electrodes so prepared are placed in a sheet-metal rack and dried for 1 to 2 minutes over a small gas flame. Dried properly in this manner the salt will form a smooth tenacious mass which uniformly covers the entire end of the rod. The electrodes may also be dried by placing them in an indirectly heated oven at a temperature of approximately 70° C. They will dry satisfactorily in this manner in about 15 to 20 minutes.

As the light-source the authors used the high-voltage A C. arc (§ 86).

Further recent techniques will be found in §§ 160. 1 to 160. 5 (pp. 209-213).

CHAPTER VIII.

TYPES OF PROBLEM TO WHICH SPECTROCHEMICAL ANALYSIS IS APPLICABLE.

Uses of Spectrochemical Analysis.

NOTHING rivals spectroscopy for detecting, without the necessity of separation, minute quantities of metals present in any element, compound, or mixture. Quantitative estimations can also be carried out with much greater speed than chemical ones, and when the percentages are small the accuracy of determination is often in favour of the spectroscopic method.

§143. Scope and Limitations.—In practice the method is usually confined to the detection of any or all of the metals, and of the non-metals : arsenic, selenium, silicon, tellurium, boron, carbon, and phosphorus. The limitation to these metals and non-metals is on the score of practical considerations, for, as Harrison (1936) has pointed out, all the elements have sensitive lines, *i.e.* lines which are in evidence when only minute quantities of the element are present. The metals and a few of the non-metals have these sensitive lines in the range of spectrum lying between 2,000 and 10,000 A., which is accessible to the ordinary quartz spectrograph working in air. The most sensitive lines of many of the non-metals, on the other hand, are of wavelengths shorter than 1850 A., at which air becomes almost completely opaque. This is why practical spectrum analysis is confined to the elements mentioned *above*, since, although very many vacuum-spectrographs are in use for physical investigations, the cost of their construction and the difficulties and expenditure of time involved in vacuum technique preclude their use in practical analysis.

Fluorine is also detectable when in combination with the alkaline-earth metals, by means of the band spectra of these compounds. Gases can be examined in vacuum tubes, although very little work has been done with them in connection with metallurgy. An account of the spectrochemical analysis of gases will be found in Chapter X.

Spectrographic work does not lend itself to odd and occasional application quite in the same way as does chemical analysis, and it may therefore not appeal to the small manufacturer, who may only employ one chemist and have few samples to examine, in the same way as it appeals to a larger concern with a laboratory and staff who have to deal with numerous samples. Further, the spectrograph cannot wholly replace chemical analysis, and where only one analyst is employed a chemist is a more essential member of the staff than would be a spectrographist ; but in any establishment which calls for the employment of several chemists the use of the spectrograph becomes fully justified.

It would be foolish to expect that access to a spectrograph will obviate the need for chemical knowledge. The head of a well-known industrial research laboratory, on installing a spectrograph in 1913, laid it down as a principle that no chemist should photograph the spectra, and that no physicist should interpret them. He was doubtless led into too absolute a statement by the temptation of a pithy antithesis, but the principle is still basically sound. On the other hand, it must not be considered as a delicate instrument only of use in research and when dealing with minute traces of impurities, nor must the technique and training for its correct use be considered suitable only for highly qualified physicists, for an intelligent youth or girl should, after two or three months' intensive training, be capable of doing most useful work under supervision.

Whilst at first quantitative results should be continually checked by chemical analysis, the agreement usually found between chemical and spectrographic estimations will gradually instil that confidence which will ultimately render chemical analysis unnecessary with a number of the samples examined.

The fact that the spectrographic examination of materials sets out to do by physical methods what was previously the field of chemical analysis inevitably leads to comparisons between the two methods. Whilst the two methods cover similar ground, they both have their respective fields of major utility, and since some work is best done by chemical analysis and other work by spectrographic examination, it is only doing spectrographic work an injustice to expect more from it than it is capable of yielding. For obtaining the relative proportions of the major constituents in any material chemical analysis must be employed, the field of spectrographic analysis being essentially that of minor constituents and impurities ; it therefore takes care of that field where chemical analysis is most difficult and unsatisfactory.

The two methods must also be applied with due consideration to their respective advantages. For example, much larger masses of the material are required for ordinary chemical than for spectrographic analysis. A sample, or the various components of a product, may frequently be examined spectrographically without damage, and although the development of micro-analysis has made possible the chemical examination of very small quantities of materials, the spectrographic method is more complete and less tedious.

A keen interest in the method can be developed by starting with relatively simple apparatus and gradually making those additions which are helpful and sometimes necessary for the full development of the method on a quantitative basis.

It is the first step in spectrographic work which is the most difficult, especially for those who have not been in close touch with it and who remain therefore somewhat sceptical, but once this first step has been taken, a full appreciation of the value of the method and its development in directions probably not contemplated at first are bound to follow.

Standards of carefully analysed samples form the basis of all quantitative spectrographic work, but in most laboratories it is not necessary for the spectrographist to be able to cover the widest field of applications, for much more commonly his interest lies in a comparatively small range of materials, and once he is thoroughly trained in this limited field, extension into wider fields is relatively simple. Literature bearing on spectrographic methods of examination is increasing rapidly, and the standardization of methods is now such that the work of the spectrographist to-day is very greatly simplified as compared with what it was ten years ago.

§ 144. Accuracy.—In quantitative estimations the accuracy depends a good deal on the nature of the substances and the percentage present. In metals and alloys, when the percentages are not large, the accuracy is within from 2 to 7 per cent., varying with the nature of the alloy and of the constituent to be determined. It may here be again stated that where accuracy is given in this book as a percentage, it is the percentage of the constituent being determined that is implied ; this is the generally accepted custom. The same kind of accuracy may be expected with liquids by employing Lundegårdh's or Ramage's method as improved by Steward (§ 75).

This accuracy is attainable only when the percentage of the substance to be detected is small. One hesitates to say in figures how small, since it varies greatly with different substances, but as a very rough indication one may place it at, say, 4 per cent. Large numbers of routine analyses to specification are indeed now carried out on steels containing as much as 13 per cent. of nickel, one of the most erratic of metals to determine. If the percentage is extremely small, one cannot use the most accurate means of measurement, and one must therefore revert to devices which yield an accuracy of only about 10 per cent. Here again, it is very difficult to state what one should mean by "extremely small" in this connection, owing to the greatly different sensitiveness of the lines of the different elements. In some cases 0·1 per cent. or even less is not too small a percentage of a constituent to determine with the full accuracy mentioned *above.*

§145. Sensitiveness.—In the flame spectra of liquids Lundegårdh states that by his method both high accuracy and high sensitiveness (0·0001 to 0·000 001M.) can be simultaneously obtained with calcium, chromium, copper, gadolinium, indium, lithium, manganese, silver, sodium, strontium, and tellurium; thus for these elements the flame is, he says, in all circumstances preferable (Lundegårdh, 1934, p. 68).

Hartley, many years ago, using a spark between graphite electrodes which were kept moistened with solutions of metallic chlorides, recorded the concentrations at which various metals were still detectable. The following may be mentioned: zinc 0·01 per cent., aluminium 0·001 per cent., arsenic 0·1 per cent. Many other examples from the work of Hartley, and of Pollok and Leonard (using a modification of Hartley's technique) will be found in the reference (Twyman and Smith, 1931), where also is a list (p. 130) giving the sensitivity of a number of metals when placed on the lower pole of a graphite arc in the form of powdered salts in a base composed of a suitable oxide of another metal such as zinc, magnesium, or calcium. The following are examples:

	One Part of the Element in from
Cobalt, platinum, silver	10^5 to 10^6.
Aluminium, lead, tin	10^4 to 10^5.
Antimony, bismuth, boron, silicon	10^3 to 10^4.
Arsenic, cæsium, phosphorus	10^2 to 10^3.

Finally, one may mention the very high sensitivity obtained with the carbon-arc cathode-layer (§ 85—*Glimmschicht*) method developed in the Institute of Mineralogy and Petrography at Göttingen under Prof. V. M. Goldschmidt (Strock, 1936). The powdered substances (minerals) are placed in a hole in the lower carbon electrode, which is made the cathode, and the spectrum observed is that of the radiation from the immediate vicinity of the cathode. The method is capable of detecting most elements down to percentages as low as 0·001 or even less.

Information on the still greater sensitiveness with the high-voltage A.C. arc will be found in § 86.

The sensitiveness of detection of most metals in the metallic state is very great. It is scarcely possible to put a limit to it, for it is rarely the case that, when excessive sensitiveness is needed in detecting a particular metal, a special method cannot be worked out to achieve it.

A complete qualitative analysis requires only an extremely small quantity of the substance. Ten milligrams is usually ample, but complete analysis (including all metals occurring to the extent of 1 per cent. or more) can be made with a fraction of a milligram. Even with these small amounts good quantitative indications of minor constituents can be obtained, sometimes in cases where chemical methods are well-nigh inapplicable owing to the small amounts involved—see, for example, Späth (1932), § 134.

§ 146. Speed.—Speed is one of the major advantages of the spectrograph, and this becomes specially noteworthy when the corresponding chemical analysis is difficult. For example, to determine by chemical methods such small quantities of cadmium and lead as are of interest in the production of high-grade zinc is very tedious. The dissolution in acid of zinc of this purity is extremely slow even when accelerated by the formation of a couple. The multiple precipitations necessary for the complete separation of cadmium are themselves lengthy and laborious operations, and the chemical analysis of such a metal takes some days for completion. Such an interval between the lifting of a sample and the time when information is available makes chemical analysis in this case quite useless for complete control, although it is still found preferable to use chemical methods for the determination of iron. In contrast, by the use of spectrographic methods it is possible for those in charge of the plant to know within 15 minutes of sampling whether the metal being produced in their plant is of marketable quality, conforming with the stringent guarantees given.

Speed may be necessary in order that a particular process may be controlled in operation ; and by rapid processing of the plates and general speeding up of technique, Vincent and Sawyer (1939) —§ 62. 1—are able to present quantitative analysis of iron for chromium, copper, molybdenum, nickel, and silicon in 8 minutes or less from pouring a specimen ingot.

More usually it is speed of a different kind that is sought, namely as many analyses as possible in a given time, where one can afford to wait for an hour or two for the result. In such cases one takes the spectrograms of a number of specimens all on the same plate. A few examples may be given :

(*a*) In the determination of iron, silicon, manganese, and magnesium in an aluminium alloy, the taking of a plate with, say, 28 exposures (10 samples, 4 standards, each sparked in duplicate) occupies less than an hour, and after developing, fixing, and drying the plate, the inspection, measurement, and subsequent simple calculations are completed in about an hour and a half.—*Government Chemist's Laboratory, London* (Candler, 1939, p. 41).

(*b*) A skilled laboratory assistant could test by chemical means 25 to 30 samples of aluminium for iron per day of 8 hours, 4 to 6 for silicon, and 3 for copper. Since the works requirements exceeded 200 samples per day during the peak season, the analytical staff were subjected to an unreasonable strain.

The adoption of spectroscopic methods led to an immediate improvement in conditions and speed of analyses. One operator can now analyse and estimate 20 samples per hour, using an internal standard.

Chemical checks over a long period have shown very reasonable agreement of results, and since deciding upon a limiting test the method has become even more rapid.—*F. C. Stephen, Telegraph Condenser Co., North Acton, England* (Candler, 1939, p. 42).

(*c*) In the laboratory where the analysis of most metals used by the British Admiralty is carried out, spectrochemical methods are now being extensively employed with great success. During 1938 approximately 50,000 quantitative determinations were made, exclusive of those connected with development work. It was anticipated at the end of 1938 that during 1939 the number would be almost doubled.—*F. G. Barker, The Bragg Laboratory, Admiralty Inspection Department, Sheffield* (Candler, 1939, p. 15).

Variety of Uses.

§ 147. Spectrochemical analysis is useful in the examination of almost every kind of substance : metals and alloys, liquids, powders, ores, soils, glasses, slags and other vitreous substances, refractories, precipitates, residues, and animal and vegetable tissues and fluids. In connection with chemical analysis alone, one may point out the great advantage which the spectroscope offers in the following operations :

(i) Rapid qualitative analysis of the whole of the metallic constituents of a substance as a basis for planning the chemical analysis.

(ii) Approximate analyses by sight (after a certain amount of experience has been obtained).

(iii) Examination of precipitates (after weighing) for freedom from constituents which should have been separated.

(iv) Detection of traces of metallic impurities or constituents in :

Inorganic precipitates, residues and powders.
Organic substances, *e.g.* foodstuffs, plant and animal fibres, textiles, etc.
Vitreous substances, *e.g.* glasses and slags.
Refractories, clays, etc.

(v) Testing the purity of analytical reagents.

(vi) Detection of rare, unexpected, or trace metals in minerals.

(vii) Analysis of substances of which only very small quantities are available, such as very thin films on the inner surface of lamp bulbs and radio-valve bulbs, inclusions in glass and in metal samples, and minute amounts of residue of unknown composition obtained in the course of chemical processes.

The most important main types of use are as follows :

A. Metallurgy.

§ 148. (i) Checking the Purity of Metals.—Many of the important industrial metals and alloys sometimes require to be of very high purity. High-conductivity copper and lead for cable sheathings are instances. In the laboratories of British Insulated Cables, Ltd., all copper cast in the form of wire-bars for subsequent drawing into high-conductivity copper wire is analysed. These analyses are made prior to the wire-bars being rolled and drawn, and form an acceptance test between the refinery and the wire mill. All incoming high-grade metals are analysed, these being principally lead, tin, antimony, zinc, copper, and aluminium.

Cable sheathings are analysed ; these include pure lead and lead alloys containing tin, cadmium, antimony, and occasionally a small but definite percentage of copper. Aluminium in the form of foil of very high purity is examined to check the purity of the supply from various sources.

Questions as to the source of a material are investigated spectrographically. For instance, a number of brands of copper are available, some from American, others from Canadian, South American, or South African sources; the spectra of many of these are characteristic, showing different amounts of various minor constituents, so that the spectrograph affords a quick and reliable means of identification.

At the Vickers-Armstrong's works at Elswick, England, large numbers of control samples of materials are analysed to see whether they comply with specifications demanding maximum impurities of the order of 0·1 per cent. of individual metals. All the materials used in the manufacture of non-ferrous alloys are examined spectrographically, comprising copper, tin, zinc, antimony, lead, aluminium, and nickel.

The Metallurgy Department of the National Physical Laboratory, Teddington, has the problem of obtaining or preparing various pure metals as starting-points for its researches on alloys, and the spectroscope is applied to the grading of possible supplies and to the control of stages of preparation. The fractionation of magnesium, for example, by sublimation in a closed tube was followed by means of spectrograms yielded by samples taken at different heights above the crucible: this method of analysis was naturally much more economical of time and material than chemical separation. Metals such as platinum, palladium, and bismuth, used by the Heat Division of the Physics Department in fixing the temperature scale, have also been examined. An elusive trouble, which occurred in connection with the purification of contaminated mercury by electrolysis and vacuum distillation, was traced by spectroscopic analysis to the presence of silver, which was carried over *in vacuo*: the gradual elimination of the silver was then followed by the same means.

§ 149. (ii) Routine Analysis to Specification.—Where large numbers of routine analyses have to be carried out on the same type of alloy, spectrochemical analysis becomes extraordinarily convenient and speedy.

As it is usually the minor constituents in an alloy which require the most skilful and lengthy separations by chemical methods the advantages offered by the spectrograph are obvious. The economy of the spectrochemical method is well illustrated in the analysis of material such as cartridge brass, where impurities are limited by specification to very small amounts. For example, the complete analysis of twelve samples of cartridge brass may occupy one analyst about a week, whereas they can be analysed quantitatively by spectrographic methods within 3 hours. The elements usually estimated are lead, bismuth, arsenic, antimony, iron, nickel, aluminium, manganese, silver, tin, and cadmium.

This type of application accounts for the great majority of spectrochemical analyses which are now made.

§ 150. (iii) General Qualitative Analysis.—In consulting practice this class of application is all-important. The manufacturer's chemist usually knows what has " intentionally " found its way into the specimens he is analysing ; the consultant usually does not, and it is the first step in his problem to know everything that is there. The former requires as a rule a strictly quantitative result ; for the latter a qualitative result, quickly obtained and free from doubt or ambiguity, is a great boon.

A qualitative analysis gives the chemist prior information regarding the product he has to examine, which is of great value in deciding how far he need carry his chemical examination. A spectrographic examination, together with the estimation of one of the major constituents, may give all the information necessary, whereas without the spectrographic examination a complete chemical analysis may be required, laborious though this is, and the presence of some minor constituent or undesirable impurity even then may be overlooked.

§ 151. A. de Gramont seems to have been the first to use spectrochemical analysis extensively for solving metallurgical problems (de Gramont, 1920).

In the publication cited he says : " Sur ma demande et par une note du 19 novembre 1916, M. le Ministre de l'Instruction Publique et des Inventions voulait bien porter à la connaissance de MM. les Ministres de la Guerre et de la Marine, de M. le Sous-Secrétaire d'Etat de l'Artillerie et des Munitions, de M. le Secrétaire-général de la Chambre Syndicale des Fabricants de matériel de guerre (en priant celui-ci d'en donner connaissance aux adhérents intéressés), que mes appareils et les méthodes que j'avais introduites en analyse spectrale étaient à la disposition de tous les services travaillant pour la Défense Nationale."

De Gramont used a qualitative method of analysis consisting of observation of the *raies ultimes* (§§ 30, 39, 112, 113), together with such quantitative estimations as could be derived from them, for the examination of a large number of materials. Among these were aluminium alloys, which he examined for the presence of lead, zinc, or amounts of iron or magnesium which might have material effects on the alloy. Other metals analysed by him were secret alloys of nickel and aluminium, various steels, including steels for artillery, large guns, and shells (including shells with which Paris was bombarded from the "Big Berthas"), and in particular the reddish deposit on the exterior of these shells. This deposit contained substances not present in the metal of the shells themselves, and was apparently a product of the intense volatilization of a copper-lead-zinc alloy without any tin. Tin and platinum were among the other substances examined by him with valuable results in comparing the French products with those of the enemy.

§ 152. Obviously there are many occasions on which a rapid qualitative analysis is very useful in a works laboratory also. It may be desired (1) to examine a competitor's product, (2) to identify a specimen which shows unexpected failure, (3) to analyse an alloy submitted by a customer as a first step to matching it, or (4) to sort a quantity of stock metal of doubtful origin. Again, in the purchase or sorting of scrap it may be useful in helping to exclude material containing some deleterious constituent.

§ 153. (iv) Inclusions, Segregation, and Gases.—In a number of works the spectrograph is used for examining small inclusions and other local defects or variations in metals. For example, at British Insulated Cables, Ltd., Prescot, England, inclusions have been found in drawn wires and particles in rolled sheet, strip, and plate. During the manufacture of wire troublesome breaks sometimes occur due to inclusions of particles of ferrous metals. It is important, of course, to determine the origin of these, and the spectrograph enables the source to be traced and leads to the number of breaks being considerably reduced.

Spectrographic analysis has also helped to throw light on a minor defect of cable sheathing, known to cable makers as "feathering." A slight but highly localized segregation was found, which had been missed by ordinary chemical analysis because the segregation occurs only close to the surface, and was difficult to separate mechanically from the remainder; in the spectrographical method, the surface was investigated by sparking without first separating it from the main body of the sample.

Gases drawn *in vacuo* from molten metals have been analysed. The sample of metal was melted in a silica tube, to which had been sealed a glass main carrying several Geissler tubes, the whole being highly evacuated. High-voltage discharge applied to the ends of the Geissler tubes showed a changing spectrum during the course of the continued evacuation of the molten metal, and at various stages the Geissler tubes were sealed off with a blowpipe flame without any interruption of the main apparatus.

At the Admiralty Inspection Department, Sheffield, spectrochemical tests have been found most useful as a means for determining the composition of ghosts and segregation in steel. This is a matter which has for a long time been of great interest to metallurgists, but little progress had been made previously, due to the difficulty of isolating the segregates from the normal metal for chemical analysis.

Small inclusions and heterogenous alloys have been studied in this way at Vickers-Armstrong's works at Elswick, where metal coatings also have been identified by the spectrograph.

§ 154. (v) **Examination of Scrap.**—This is a very useful application ; an illustration is given in the section on lead (§ 205).

§ 155. In this chapter we are not concerned with the types of instrument or ways of using them, but it is convenient to point out here that although all the foregoing applications are customarily carried out by means of the spectrograph, yet there are occasions on which a specialized form of the older instrument, the spectroscope, known by the trade-name of *Steeloscope*, is much used for the rapid examination of scrap, the sorting of alloy-steel bars, and so forth (see § 202).

A similar instrument to the above was later developed by Landsberg, Mandelstam, Tuljankin and Zehden (1935) for a similar purpose, while an improved version had a mechanism for passing through the spectrum (Mandelstam, Smirnow and Zehden, 1936). A quite different type of spectroscope, however, was employed by Mandelstam, Ra'skij and Zehden (1936) for the rapid determination of silicon and chromium in malleable cast iron ; it was used with the spark, and had two fixed eyepieces, one in the red, the other in the violet region, the former being provided with a polarization photometer. All three instruments were developed and constructed in the optical laboratory of the Physical Institute of the Moscow State University.

B. Substances not in the Metallic State.

Although this book is about the spectrochemical analysis of metals and alloys, one must remember that both spectrographs and those used to working with them are still few and far between, and their services are often sought for in other than metallurgical problems. I have thought it well, therefore, not to exclude these applications entirely.

§ 156. (i) General Industrial Problems.—The applications to industry are so very diverse that it would be waste of time to attempt any systematic arrangement in this chapter.

We find in one laboratory that the spectrograph is applied to the examination of a great variety of non-metallic stores, including paints and paint pigments, varnishes, drying oils, lutings and their ingredients, asphalts, fabrics, rubber, etc. From the point of view of safety in connection with the use of certain explosives some of these products must contain not more than severely limited traces of certain metals or their compounds. The objectionable metals are non-volatile in character and generally may be readily determined by chemical methods in the materials or the residues from them after careful ignition and incineration. Chemical methods, however, are relatively laborious and time-consuming, an average sample requiring some 4 to 5 hours' manipulative time spread over a period of 2 days. The use of the spectrograph materially reduces the manipulative time necessary and greatly expedites results.

In other laboratories actual paint films are examined to discover whether failure is due to faults in the materials ; stoving enamel is examined to detect the driers used (usually the cobalt, manganese, or iron salts of various organic acids) ; qualitative analyses are made of frits, enamels, ashes, and precipitates obtained in chemical analyses.

In laboratories concerned with dielectrics the composition of mica has been related to its electrical properties, the metallic coatings of dielectric materials have been identified, and traces of metallic compounds detected in insulating oils.

In connection with brewing many uses have been found :

" A great variety of materials have been used for the construction of plant or equipment for the manufacture, transportation, and service of beer. The question of the suitability of these materials from the point of view of metallic contamination is of the utmost importance. Beer, at some stage during its manufacture, may be in contact with copper, copper alloys, iron, steel, lead, tin, nickel, aluminium, glass, enamels, stone, slate, wood, and possibly other materials. Quite apart from considering whether the product has taken up metals in such amount as to constitute a danger to health, there is another important aspect, namely, the effect of the dissolved material on the flavour and appearance of the beer. . . .

" The spectrographic method has been found particularly useful for this type of work. A qualitative survey may be made on a few milligrams of the ash of the sample or on small precipitates, or residues obtained in the course of chemical analysis. Quantitative estimations of one or more metals occurring together may be made on the same spectrogram. . . .

" In addition to the examination of the finished beverages, it has been of value to make tests of raw materials and of the product at various stages of production, for example, wort, sugar, hops, and yeast.

" Constructional metals and alloys have been examined qualitatively.

" Tests made to determine whether the various metals are dissolved show that in many cases undesirable amounts are entering solution whilst no visible indication of corrosion is apparent. Similar investigations have been carried out with glass bottles and glazed containers.

" Other applications in addition to the above have included the control of raw materials and products for deleterious constituents in various industries, including sundry materials such as deposits, incrustations, sludge, and corrosions, particularly when only small samples such as scrapings are available.

" In certain investigations of the effect of traces of elements in biological or enzymic processes, bearing in mind the minute amounts that are of significance, the spectrograph has proved indispensable.

" In the general analytical laboratory, a spectrographic test prior to ordinary chemical analysis will often give valuable information enabling the chemist to devise a suitable technique, especially for the minor constituents."—*Communication from Murphy and Son, Ltd., Wheathampstead, Herts., England* (Candler, 1939).

§ **157.** (ii) **Minerals and Ores.**—Ever since the discovery of rubidium and cæsium by Bunsen and Kirchhoff in 1861, spectrochemical analysis has provided an unrivalled means of detecting the various minor elementary impurities which occur in minerals, rocks, meteorites, and natural waters. Especially has it been of use in those cases where ordinary chemical and microchemical methods could not be employed, either by reason of the insensitivity of such methods or of the scarcity of material. For many years qualitative spectrochemical analysis of minerals was practised with considerable success by A. de Gramont in France and Hartley and Ramage in Dublin, and many examples of analyses by these and later workers up to Fitch (1931) will be found in the last-named reference.

Academic mineralogists have shown a very great interest in detecting traces of metals in minerals, and this has been brought to great refinement by Professor V. N. Goldschmidt and his coworkers at the Mineralogical Institute of the University of Göttingen, mention of whose work has been made in §§ 85 and 145. But of greater interest to the metallurgist are two other applications : one in prospecting for new sources of metals, and the other to the testing of ores for minor metallic impurities which might be injurious if passed through into the refined metal.

In connection with prospecting, very interesting work has been done by the examination of the soil of river beds, in which traces of metals will be found brought down by the stream. The prospector, on arriving at a branch of the stream and examining the river beds of the respective tributaries, finds more of the metal he is seeking in one than in the other, and so is eventually guided to the desired metalliferous district.

An instance of the examination of ores for objectionable constituents is found in the search for bismuth in copper ores. Even in deposits where the ore contains bismuth, the content varies from place to place, and considerable advantage may be derived from reserving for high-conductivity copper those portions of the deposit which are relatively free from bismuth.

It has been found possible to employ the data afforded by spectrograms for purposes of correlation, a comparison being effected not only by the presence or absence of particular minor impurities, but also by the approximate amounts in which they occur, this being inferred from the intensity of their respective lines. Thus spectrograms of the biotite occurring in a series of basic lavas of the Permian age in Devonshire showed that a marked similarity existed between certain members of the series, and a correlation was made which was in accord with the conclusions arrived at by a purely petrological study of these rocks.

§ 158. (iii) Plant and Animal Tissues.—Of recent years it has been found that there is an important connection between traces of certain metals in the soil and both the growth of plants thereon and the health of animals feeding on those plants. In this connection the spectrograph has become of very great help in tracking down the causes.

In recent years the widespread nature of mineral-deficiency diseases of animals has been recognized. A disease of sheep known in New Zealand as "enzootic marasmus" or "bush-sickness" and in Australia as "coast disease" was found to be curable by moving the affected animals to lowland pastures. Further investigation showed that dosing sheep with crude iron salts or with acid extracts of soil from recovery pastures could prevent or cure the diseases, and the element responsible was finally found to be cobalt, of which 1 mg. per sheep per day was sufficient.

In this country similar diseases are known in Scotland (Sutherlandshire and the Cheviots) and Northumberland under the name of "pine," in the Peak District of Derbyshire as "warfa" or "swayback," on Dartmoor and Exmoor as "pine" or "moorcling," and in North Wales. Corner and Smith have recently shown that "Border pine" in the Cheviots can be cured by the administration of 1 mg. of cobalt per day, and Dunlop and Wells have shown that copper will control swayback. As far as work in progress goes the Dartmoor "pine" is similar to "bush-sickness." The work has been re-opened, and spectrographic examination of soil and grass samples is in progress.

A "disease" of cattle, known as "teart," occurs in Somerset, and is more or less closely associated with the Lower Lias. Spectrographic examination of teart and non-teart herbage showed the former to be higher in molybdenum content. If the investigators had been limited to chemical methods of analysis, it might have been a very long time before this difference in molybdenum content was spotted.

The importance of certain elements in minute quantity for the healthy growth of plants has been shown in recent years to be of considerable economic importance. Among others, boron is essential for broad-beans, swedes, turnips, sugar-beet, cauliflower, celery, potatoes, and many other plants of commercial value. Lack of this element causes brown heat of swedes and root crops, and is controlled by the application of about 20 lb. of borax per acre.

Internal cork of apples has been known in New Zealand for fifty years. The symptoms are somewhat similar to those of bitter-pit, which occurs also in this country, but the two diseases are distinct. Examination of the ash of apple pulp and leaves from healthy trees and trees affected with bitter-pit and corky core, sampled in various districts in this country, is being made spectrographically for boron.

Again, the spectrograph has been used to demonstrate the distribution of both potassium and rubidium along the axes of unbranched roots of such plants as barley.

The same technique, save that an oxy-acetylene flame was employed, was successfully operated in the laboratory of the Carnegie Institution of Washington at the Dry Ortugas off the coast of Florida, even under trying conditions in an isolated situation in the tropics. There organisms grow which are unusually well adapted to the investigation of salt absorption, and the spectrographic method made possible an accurate quantitative comparison of the uptake of the different alkali metals. The results have considerable importance relative to the still unsolved problem of how plants accumulate certain ions which are only supplied at great dilution.

The analysis of soils for their major constituents such as the alkali metals, etc. has been brought to a high stage of perfection by Lundegårdh (1934).

§ 159. (iv) **Art, Archæology, and Criminology.**—These applications are associated together because they have a good deal in common. In all three it is highly important that, if an analysis of a specimen is required, it should be made practically without destroying any appreciable part of the object investigated.

To the art historian the analysis of inorganic pigments and the inorganic bases of lakes are subjects of frequent interest. The analysis of antique glasses and pottery is also very conveniently made by the spectrograph, which, in addition, has been applied to the often obscure materials excavated by archæologists. In the study of museum specimens, gold, silver, bronze, copper, and tin coins, speculum metal, pewter, and lead have all been examined, with results more comprehensive in character than could be expected from microchemical investigation. When precautions are taken to prevent overheating, no damage results to the object under test, and a permanent record is obtained which can be filed for reference (Bergsøe, 1937 and 1938).

The spectrograph has recently been much used in forensic science.

The fact that two samples of paint are, for example, lithopone paints is not of much value as evidence, but if it can be shown that one sample contains in addition a trace of antimony, while this is absent from the other, a common origin for the two samples is excluded, and valuable information has been gained. Again, all brasses contain copper and zinc, but if each of two specimens is found to contain also approximately equal, but small, amounts of the same other elements, such as lead, nickel, cadmium, and manganese, a strong presumption of the identical origin of the specimens is created. This presumption is stronger still if these minor constituents are such as do not commonly occur in brass, say antimony and chromium.

An interesting case in which a spectrographic analysis of paint was useful was one in which a quantity of ashes of an unknown fabric was submitted for examination in order to determine whether, if it had come from a painting, this painting could have been an " Old Master." A preliminary examination of the material showed that the original fabric had certainly had the texture of canvas, and that associated with the burnt fabric was a quantity of what might well be incinerated oil-paint. This substance was then analysed. It was, of course, realized from the outset that the result might be inconclusive—*i.e.* the composition of the material might be consistent with its having been a paint of a kind employed both in the Middle Ages and to-day, *e.g.* white lead. Actually, however, analysis showed that the material consisted mainly of a titanium compound. Hence the ash may have been that of a paint (titanium oxide), but this paint could certainly not have been applied in the Middle Ages, nor even before about 1920.

§ 160. (v) Analysis of Organic Chemicals for Traces of Metallic Impurities (Hess, Owens and Reinhardt, 1939).—" Rapid, accurate analysis for small traces of metallic impurities is an important factor in the manufacture of modern organic chemicals. For this reason the spectrochemical analysis of such materials, including cellulose derivatives, synthetic resins, pharmaceuticals, dyes, and biological tissues and fluids, has been developed for traces of aluminium, calcium, copper, iron, lead, magnesium, manganese, nickel, strontium, tin, and zinc. The determination of some of these elements in the presence of others, in their natural range of abundance, is very difficult, if not impossible, by chemical methods. The spectrochemical method is not thus limited, and gives good precision in the low-concentration range of interest. Moreover, the spectrochemical analysis effects an important saving of time, since the analyses for all the test elements may be carried out by measurements made upon one spectrum . . . "

A great many of the above illustrations have been derived from Candler (1939), who refers to the work done in Great Britain. How widely the spectrograph has been applied to industry in America, France, Germany, and other countries may be seen in Chapters VII and IX.

§ 160.1. Variant-exposure Method (McClelland and Whalley, 1939).—These authors describe a method of quantitative analysis in which a series of exposures of different duration are made for each sample. They call this the "variant-exposure method."

§ 160. 2. Direct Photometric Spectrophotometry (Thanheiser and Heyes, 1939).—A method of spectrochemical analysis by means of direct, simultaneous, photo-electric measurements of two spectral lines in the spark is described. The apparatus consists of two monochromators which are simultaneously illuminated by the spark. One monochromator is set for the main-constituent line, the other for the line of the element to be determined. Behind the exit slit of each monochromator there is a photocell, each connected to a separate electrometer. During the exposure a certain charge is accumulated on each electrometer. From the ratio of these charges the concentration of the element in question is determined by means of a standard curve. The average error of the method itself (consistency) if both monochromators are set for the same line is 1·5 per cent.

Experiments with copper determination in aluminium were not satisfactory for copper percentages over 0·2, since the charge ratio then increases very slowly with increasing copper concentration.

Magnesium and manganese determinations in aluminium (Al 2816, Mg 2791, and Mn 2949 A.) gave satisfactory results. The accuracy is about the same as that obtained with the photographic method.

The authors admit that for the time being the apparatus is not suitable for routine work.

§ 160. 3. Quantitative Analysis by Measurement of the Widths of Lines (Gerlach, Coheur and Coheur, 1940).—This paper consists of a critical study of a proposal put forward by Gerlach and Rollwagen (1937*a*, 1937*b*).

The authors base their measurements on the fact that spectrum lines have a measurable width. The intensity of the line of the constituent is compared with that of the basis metal by measuring the width of the latter between the points at which its blackening is equal to the peak blackening of the former.

The paper is a very thorough one (143 pages), and a good case is made for the serious consideration of this method of working.

§ 160. 4. Boron and Molybdenum in Grass; Synthesis of Artificial Plant Material (Ashton, 1940).—Apart from the addition of an internal standard, the grass to be analysed was given no previous treatment before being burnt in the D.C. arc. Copper electrodes were used for the determination of boron and graphite ones for the determination of molybdenum. Fifty parts per million of gold and 200 parts per million of platinum were found to be satisfactory as internal standards for boron and molybdenum respectively when the lines B 2498, Au 2428, Mo 2816, and Pt 2830 A. were used. The densities of the lines were measured with a microphotometer, and the ratios—galvanometer reading for the internal standard : galvanometer reading for the element—determined. For the construction of graphs standards were prepared by adding the internal standard and increments ranging from 0 to 1000 parts per million of boron or molybdenum to a "synthetic grass," a mixture made up to resemble as far as possible the composition of grass.

The preparation of the "synthetic grass" offered considerable difficulty. The density of an arc-spectrum line is influenced not only by the concentration of the element emitting it, but also to some extent by every other element, radical, and compound present in the substance emitting the spectrum. Silicon was found to be one of the most active elements in this respect, while the nitrate, sulphate, and chloride radicals all had characteristic influences. With the internal-standard method, each member of the pair of lines was found to be influenced to a different extent, with the result that the ratio between their densities was greatly affected. A satisfactory "synthetic grass" was eventually prepared by grinding up the following substances together in a large pestle and mortar :

	Grams.
Potassium hydrogen tartrate	22·70
Di-ammonium hydrogen phosphate	2·57
Calcium lactate	8·91
Magnesium sulphate ($7H_2O$)	4·53
Sodium sulphate (anhydrous)	0·24
Barium sulphate	0·03
Magnesium sulphate ($4H_2O$)	0·13
Silica	13·60
Ferric chloride ($6H_2O$)	0·27
Aluminium oxide (calcined)	0·80
Urea	8·50
Ammonium chloride	0·85

When these had been thoroughly mixed, they were added to the following mixture :

	Grams.
Soluble starch	68
Sucrose	5
Casein	33·5
Carnauba wax (previously ground)	8
Whatman No. 1 filter-paper	32·4

The filter-paper was ground to a fine fibrous powder in a Christie and Norris mill. After the two mixtures had been mixed together, they were reground in the same mill.

In order to prepare the standards, 10-g. portions of the mixture were weighed into porcelain basins, and portions of solutions containing the internal standards and various quantities of boron or molybdenum were added to them by means of a pipette. They were then dried in a steam-oven and, when dry, ground in the Christie and Norris mill, thoroughly mixed, and then transferred to reagent bottles.

§ 160. 5. Correlation Method for the Elimination of Errors due to Unstable Excitation Conditions (Levy, 1940).—The author, seeking a method which does not demand strict uniformity of sparking conditions, electrode shape, closely approximate proportions of other alloyed substances, etc. (which in practice cannot always be obtained), develops the procedure suggested by Naedler (1936).

In his summary Levy says :

" Some difficulties associated with quantitative spectrum analysis cannot be removed through improvements in equipment only.

" A survey of the most important light-sources for quantitative spectrum analysis shows that the radiation of all of them is determined by only one quantity, which is either the gas temperature or the electron temperature, the latter of which is in some cases higher, in others equal to, the gas temperature of the discharge. The excitation energy is therefore distributed among the excited states of the atoms statistically, and the number of atoms in the various energy levels is determined uniquely by the electron or gas temperature. Consequently the intensity ratio of two lines is related to the intensity ratio of two others. A ' correlation method ' is described, which permits one to work at non-standardized conditions (variation of the shape of the electrodes, influence of extraneous elements, etc.) while reducing the measurements to ‘normal’ (standard) conditions. The method may also be profitably used under standard conditions to improve the accuracy of an analysis while eliminating errors due to accidental fluctuations in the light-sources.”

This paper is interesting ; but the theoretical treatment seems too simple to be adequate.

The investigation is so far theoretical ; it is to be hoped that Dr. Levy, an experienced spectrochemist who played a considerable part in the establishment of spectrochemical analysis in the U.S.S.R., will carry his investigations further and try his method in practice.

CHAPTER IX.

THE PRACTICE OF SPECTROCHEMICAL ANALYSIS OF METALS AND ALLOYS.

N.B.—The sections following the Introduction deal with the determination of the elements in the metals and alloys named at the head of each section, and are arranged in alphabetical order.

INTRODUCTION.

§ 161. In the foregoing chapters we have considered the separate procedures which go to make up the conduct of a spectrochemical analysis. A few general notes on procedure will be given before describing the way in which different workers deal with specific metals and alloys.

§ 161. 1. The "Standard" Method.—A good practical routine of general all-round utility is described in § 165 in its application to aluminium alloys. We may refer to this routine as the "standard" method, without in any way implying that it is the only or the best practical one. The alloys to be dealt with, the character and layout of the whole works, and other special factors must in each case determine which is the best method to employ; but if provision is made for the "standard" method, any alterations which have to be made, as for instance the provision of supplementary apparatus, will not entail waste of money.

The reader is strongly recommended to obtain the valuable pamphlet, *Quantitative Spectrographic Analysis with the Microphotometer* (Smith, 1939), and to consult it on all matters referred to in the table of contents which will be found in § 71.1 of this book.

Factors involved in attaining Quantitative Accuracy.

§ 161. 2. Maintaining Constant Conditions.—Certain factors can be varied without much alteration in results. For example, with certain alloys no error is introduced by making such variations in the spark gap as from 2 to 4 mm. On the other hand, it is just as easy to maintain constant conditions as not to do so. The reader is referred to § 192 for suggestions on this subject.

§ 161.3. Heterogeneity and Presparking.—One may distinguish four kinds of heterogeneity: macroscopic; microscopic (*e.g.* having a crystalline or granular structure); that due to oxidation, fusion, or volatilization produced by the action of the arc or spark; and segregations such as those to which Barker draws attention (§ 197).

So far as the spectrograph reveals local differences of concentration of constituents, it is informative. If it should be desired to sample a considerable area, moving electrodes may be tried, but neither in my laboratory nor in that of Barker (*loc. cit.*) has this method been helpful in removing such discrepancies as are met with in uniform specimens.

The nature of what takes place in sparking material which has a grain was set forth by Gerlach and Schweitzer (1931*a*) and named by them the "grain-boundary effect" (*op. cit.*, p. 114). The authors say: "As a specially interesting case of the application of local analyses we may mention the spectrographic proof that lead present as impurity in gold is deposited for the major part at the grain boundary, and thereby gives rise to the brittleness of gold containing lead. When, for instance, a specimen of gold containing 1 per cent. of lead was fractured, the content of lead in the first spectrogram taken from the fresh fracture was invariably many times greater than that obtained from a cut specimen. Very short exposures of a few seconds taken from fresh fractures exhibited even an excess of lead over the gold. When a more extensive series of spectrograms was photographed, the intensity of the lead lines diminished and finally became constant [Figs. 49, 50, and 51 of reference]. The constant amount was, however, exactly the same as that exhibited by the cut specimen. The difference between a fractured and a cut electrode became less pronounced with decreasing contents of lead, which is in keeping with the smaller decrease in the intensity. When the lead content is only a few hundredths per cent. the difference vanishes."

Oxidation and other changes occurring during the passage of the arc or spark differ very much according to the material being analysed, and are best left to be dealt with in the sections dealing with the individual metals and alloys. The question of segregation scarcely comes within the scope of this book.

By "presparking" is meant a preliminary period of sparking prior to the exposure of the photographic plate, the object being to attain a constant condition of the spark. Quoting Smith (1939): "During the initial period the character of the discharge varies, after which it becomes steady. This phenomenon, which is usually accompanied by changing appearance and 'note' of the spark, has been studied in some detail by German spectroscopists, and was first described by Töpelmann and Schuhknecht (1931) as the *Abfunkeffekt*. In the absence of an equivalent English phrase, van Someren suggests the term 'sparking fatigue'; its characteristics are detected when successive exposures (of short duration) are made of the spark without interrupting it, and the relative intensity of a pair of lines of the basis and alloying metals is plotted against time."

Fresh light is thrown on the question of presparking by Mäder and Poetzelberger (1939), as will be seen from the following abstract:

> Microscopic examination of polished metallic surfaces on which a single multiple spark has played shows that, with feeble sparks which attack only the actual surface of the metal, each individual spark melts out of the metallic surface a recess, and then evaporates the molten metal therein. At the bottom of the trough there remains a bright, highly reflecting surface from the molten metal. After repeated sparking in the same place, the spark strikes into the already fluid metal, flinging the metal outward, and the latter lies in the space around in the form of spherical and partly oxidized drops. The spark continues to play on the melt and not on the drops, penetrating further into the metal.
>
> "Slag" or a so-called "film of oxide," which according to various publications must be pierced by the spark, appears only with higher currents.
>
> When, in beginning to spark an aluminium alloy containing, say, 7 per cent. of magnesium, a temperature is reached at which a liquid alloy is produced, then, as can be seen by reference to the phase diagram of aluminium-magnesium alloys, the liquid is richer in magnesium than the main alloy itself. Again, when vaporization begins, the vapour produced is richer in magnesium than the fused metal. (The authors illustrate these points by phase diagrams.) It is to the successive impoverishment of the magnesium during sparking that the authors

> attribute the lowering of the intensity of the magnesium line as compared with the aluminium line, *i.e.* the change which when plotted on a time-scale is called by the authors the *Anlaufkurve* ("presparking curve"). Thus the vapour developed by the spark from a Hydronalium specimen is at first richer in magnesium than corresponds to the true proportion of the alloy, and only in so far as the electrode melts subsequently and then vaporizes through an increase in temperature will equilibrium occur in the composition of the vapour. It is at no time certain that the concentration of the magnesium in the vapour is the same as in the alloy.
>
> If one considers the presparking curve (*Anlaufkurve*) of the various metallic constituents in general, those with a lower vaporization-point, such as the solvent metal, commence with too high a value and show a falling presparking curve; those with a higher vaporization-point begin with too low a value and show a rising curve. From the sparking curves of a series of alloys the authors confirmed that this is so in most cases . . .
>
> Disagreements with this rule occur mostly for FeII, which in brass and copper alloys RE, A_3, B_3 shows a falling curve; MnII in Monel alloys, aluminium-bronze, RE, A_3 is too low. These, however, are cases in which a spark line is compared with a copper arc line.
>
> The authors confirm their conclusion by an experiment with molten alloy, Hy 25, in which they find no initial sparking effect.

This analysis of the phenomenon is interesting; it cannot be said, however, that it adds anything directly helpful to practical analysis.

Practical analysis is based on the justified assumption that the spectra obtained from two equal or very similar samples (the unknown and the standard sample) are equal or very similar, and one does not care whether the composition of the vapour is different from that of the solid alloy. The only important point is that the two samples give the same vapour composition.

From the theoretical point of view one may add that if one has an alloy in the three phases (solid, liquid, and vapour), which are in contact with each other and in equilibrium, then, of course, the concentrations are in general different and are determined by the phase rule. In the spark, however, where a little bit of metal suddenly becomes molten or vaporized within a very short time and under turbulent conditions, it may be doubted whether there is any "phase equilibrium," and consequently whether those phase diagrams give a correct description of what is actually happening. The experiments with the molten alloy also are not very convincing, as there are no details given about all the other sparking conditions.

§ 161. 4. Conclusions as to Presparking.—Diverse opinions are held on the part which is played by heterogeneity and the other factors which may cause error and uncertainty in analysis (see §§ 87. 1, 135, 137, 138, 141, 142, 168-169, 193-197, 211, 230, and 235). The reader will also find in the literature considerable diversity of opinion as to the length of time during which specimens should be presparked in order to secure the greatest consistency in the results.

Anyone who considers the complexity of the phenomena involved may well feel uncertain as to the best course to pursue, but three conclusions seem to emerge from examination of the evidence available :

(1) Macroscopic heterogeneity can be dealt with only by examination of different parts of the specimen, and any differences between chemical and spectrochemical determinations arising from this cause cannot be regarded as faults of the spectrochemical method.

(2) Where the alloy has a crystalline structure it would appear to be desirable that the area of sample from which metal is vaporized by the spark should be larger than the average area of a grain. Chill-casting or cold-working of the metal produces a desirable structure from this point of view.

(3) It seems obvious that many of the investigators, including Mäder and Poetzelberger, attach too much importance to arriving by presparking at a constant relation between the *intensities* of the lines compared. Experience shows that the longer the initial sparking, the less sensitive the method becomes. What is important is not that the ratio of the line intensities should be constant, but that the percentages implied by the measured intensities should be so. This often means that with a very short presparking time at least as good, and sometimes better, results are obtained as with the long presparking that has been advocated by some of those very workers who have added most to our knowledge of the phenomenon. Provided the same routine is strictly adhered to it is not necessarily a drawback that one should photograph the lines during the early part of the sparking, even though their

relative intensities vary during the time of observation. The result, *expressed in terms of percentages,* is often found to be as constant during the period when the intensities of the lines are changing as at a later stage when they have become almost constant, since a change of intensity in the latter case corresponds with a greater difference in the percentage of the constituent concerned than does a like change of intensity in the earlier stage.

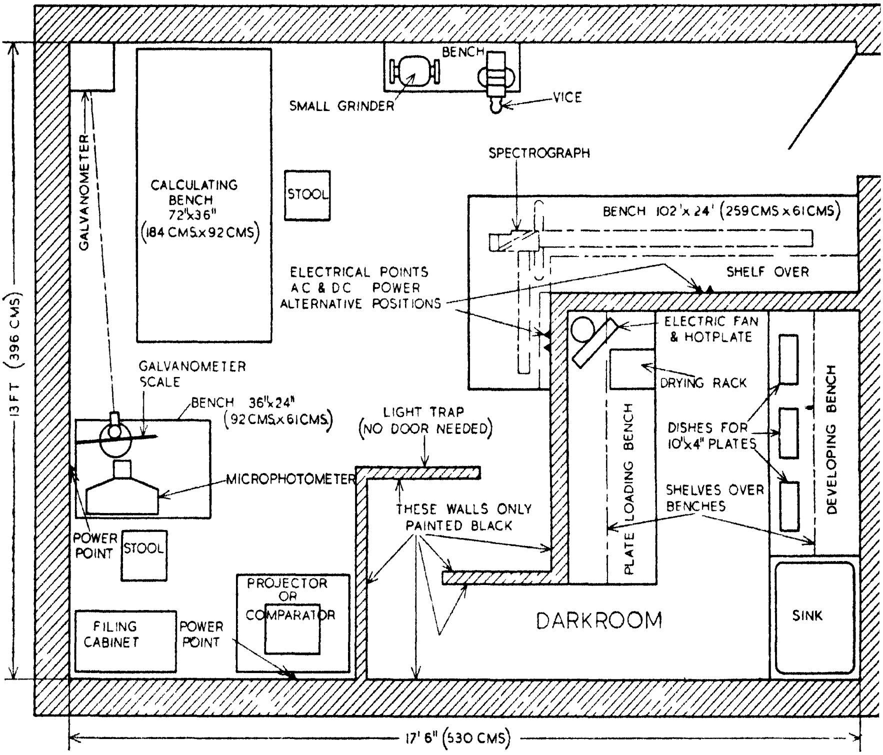

Fig. 40.—Suggested Layout of Spectrographic Laboratory.

§ 161. 5. Spark Generator.—The informative papers of Kaiser on the Feussner type of spark apparatus, the rapid, speedy, and accurate results published by Vincent and Sawyer, and the paper by Pfeilsticker predispose one to consider that to obtain the best results it is necessary to employ some form of interrupted discharge. Yet, on the other hand, we have the evidence of Bauer (§ 169), Frommer (§ 168), Handforth (§ 168), and Moritz (§ 168. 1), who did not derive any advantage in the analysis of the alloys in which they were interested from the use of such devices. There has naturally been a great deal of interest in this subject in my laboratory, and our own experience seems to show that a way can always be found in the analysis of a given alloy to obtain with the simple standard sparking outfit a result as good as any using an interrupter that have been published.

An advantage is found in certain cases in the use of the tandem spark, a very simple device with which the same kind of control can be obtained over the discharge as with the interrupted spark. This is described in § 89.

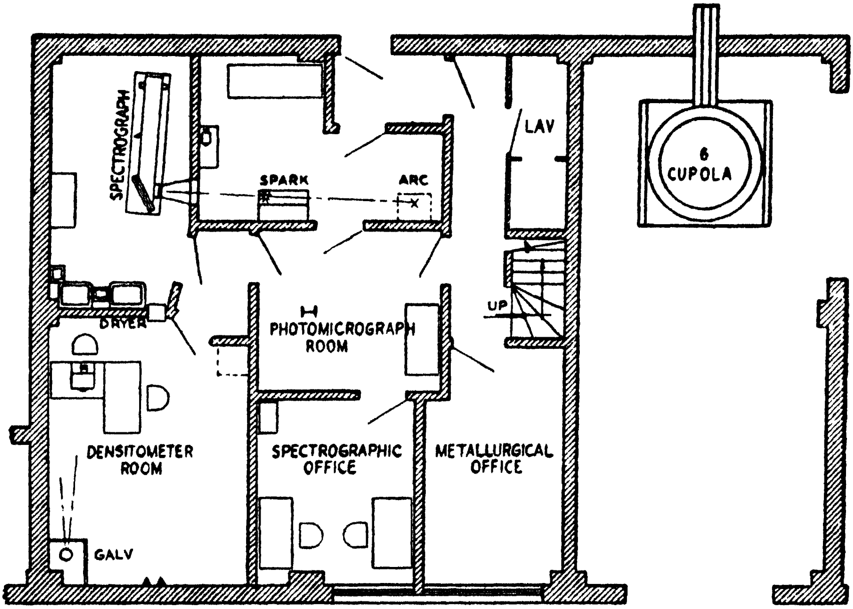

Fig. 41.—Layout of Spectrographic Laboratory attached to an Iron Foundry. Note proximity to the line of furnaces whose output is analysed.

§ 161. 6. Layout of the Laboratory.—Figs. 40 and 41 show two plans for the layout of a spectrographic laboratory, which may be useful as hints to anyone starting this kind of work.

In Fig. 40 the layout depicted has been arranged for an automatic large quartz spectrograph. If a medium quartz spectrograph is used it will be necessary to move the light-source to a point nearer to the main entrance in the layout, and the alternative power outlets have been shown for this reason. When using the large spectrograph the source is situated on that part of the bench which points towards the dark-room entrance. The layout can be modified to suit the peculiarities of the spaces available.

Fig. 41 is from the paper by Vincent, Sawyer and Sampson (1938).

The laboratory should preferably be located in the part of the works most convenient for the reception of specimens for test. With most modern spectrographs it is not essential that the room should be free from vibration. The spectrograph should be so rigid that normal vibration does not affect it.

The laboratory may have normal illumination. It is only necessary that the scale of the galvanometer should not be directly illuminated.

The dark-room may be illuminated by any good safelight. The arrangement most practical is to have the walls and ceiling whitened, and to employ indirect illumination. The light can then be of a sufficient intensity for comfortable working without there being any risk of fogging the plates.

Both D.C. and A.C. supplies should be available.

ALUMINIUM AND ITS ALLOYS.

Checking Purity.

§ 162. Although the aluminium alloys of greatest industrial importance do not call for a high degree of purity in the aluminium, there are occasions when it is necessary. For example, small traces of impurities have a great effect on the anodic formation of aluminium, the speed of which is almost a linear function of the iron content, with secondary effects due to silicon and copper. I am indebted for this information to Dr. F. C. Stephan, of the Telegraph Condenser Company, Ltd., North Acton, England, who says :

" The anodic formation of aluminium is the essential process in the manufacture of electrolytic condensers. Under well defined conditions of current density and concentration of electrolyte a highly insulating film of γ-alumina is formed into the aluminium surface.

" The formation proceeds smoothly and rapidly with aluminium of 99·99 per cent. purity, and the film produced on such metal gives a very minute leakage current when a D.C. supply is applied with the correct polarity and at a voltage somewhat lower than the primary anodizing voltage.

"For example, aluminium of 99·99 per cent. purity is anodized in a solution of borax and boric acid by applying D.C. Initially the voltage across the cell is zero, but as anodization proceeds, the current falls and the voltage rises. In practice the current is kept constant until the required voltage is reached. At this point, the current is gradually reduced but the voltage remains constant, until finally the minimum current is applied just sufficient to keep the voltage constant.

"This minimum current is known as the leakage current, and is a measure of the perfection of the anodic film of oxide.

"For a given electrolyte there is a maximum voltage beyond which the anodic film cannot be formed, and this is easily determined by sparking at the anode in the solution. This voltage—the sparking voltage—is primarily a function of the electrolyte, but some secondary effects are due to the purity of the aluminium.

"Any attempt to increase the voltage above the sparking voltage will only result in a greatly increased flow of current.

"The aluminium is therefore anodized to just below the sparking voltage, and kept at this until the leakage current is at a minimum.

"The purity of the aluminium has a profound effect on the speed with which the final voltage is reached and on the leakage current.

"Certain impurities have an inhibiting effect on film formation, and consequently strict control must be exercised over them. The chief impurities encountered are iron and silicon, of which iron has the greater effect.

"Iron can be tolerated up to 0·07 per cent. and even up to 0·12 per cent. provided a high-voltage formation is not required, but the leakage current increases rapidly as the iron content exceeds 0·07 per cent.

"Silicon can be tolerated up to 0·10 per cent.

"In practice these two impurities, iron and silicon, are estimated by means of the spectrograph, check chemical methods being employed once a week.

"Two pieces of the aluminium foil are rolled up pencil-shaped and used as electrodes. The arc is struck and an exposure given for 10 sec.

" On the same plate, a similar exposure is made using an aluminium standard which has been carefully analysed by several methods for iron and silicon content.

" After development and washing, the plate is examined, without drying, by projection giving approximately 4 times linear enlargement. Visual examination of the iron lines in the 2400 A. and 2600 A. region and silicon lines in the 2500 A. region shows whether these impurities are below the required limits.

" Since only a limiting test is required the accuracy obtained is quite adequate."

One operator samples, prepares the electrodes, and exposes 20 samples per hour, and also examines the spectrograms within that time.

Other impurities that may be of interest when present to less than 0·1 per cent. are calcium, copper, titanium, manganese, magnesium, zinc, lead, tin, cobalt, nickel, chromium, tungsten, boron, and sodium, and all of these can be determined spectrographically.

§ 162. 1. In an aluminium arc there is a great deal of background due to oxidation of the aluminium (§§ 41, 72, 83, 86), and thus the spark is in practice as sensitive as the arc, and is certainly sensitive enough to reveal all the impurities which are of industrial consequence. Thus the method of examination for impurities can be just the same as the procedure recommended for the routine spectrochemical analysis of aluminium alloys (§ 165).

§ 163. The following is a typical analysis of a batch of high-purity aluminium using the arc (Hilger, 1935*a*).

Qualitatively the metal was examined by the arc using a medium quartz spectrograph, fragments of the metal being placed in the arc between electrodes of pure silver or pure copper.

The current with the copper electrodes was 3·2 amp., the voltage across the arc being 35 ; with the silver electrodes the current and voltage were 3·2 amp. and 30, respectively. The light was focussed on the slit.

The only impurities present in significant quantity were found to be magnesium and iron, which were determined by the ratio quantitative arc method (§ 115), and silicon. The other impurities, given in Table IX, were present in much smaller amount.

TABLE IX.—IMPURITIES IN HIGH-PURITY ALUMINIUM.

Element.	Remarks.	Lines in Evidence, A.
Calcium	Practically absent. A minute trace is indicated in one spectrum only, using silver electrodes. None indicated using copper electrodes, but the continuous light might mask a minute trace.	4226·731 3968·465 3933·664
Copper	Very slight trace indicated in only one out of the two spectra.	3273·967 3247·550
Iron	0·002 per cent.	3581·197 3570·102 2973·236 2966·902
Lithium	Minute trace in one spectrum only.	6707·86
Magnesium	0·002 per cent.	2852·12 2802·69 2795·53
Silicon	Slight trace indicated by two principal lines only in one spectrum, and a minute trace by one line only in another.	2881·59 2516·12
Sodium	Very slight trace indicated by *raie ultime* only.	5895·932 5889·965
Tin	A minute trace indicated by the *raie ultime* only, when using copper electrodes, but not with silver.	2839·98

Gallium was critically sought in all six spectra and found to be quite or practically absent; there was doubtful indication of a minute trace in one or two spectra.

Degree of purity: over 99·99 per cent.

Other elements specially sought in the spectra with negative result were

antimony,
arsenic,
barium,
beryllium,
bismuth,
boron,
cadmium,
cæsium,
carbon,
chromium,
cobalt,
gallium,
germanium,
gold,
indium,
lanthanum,
lead,
manganese,
mercury,
molybdenum,
nickel,
phosphorus,
potassium,
scandium,
silver,
strontium,
thallium,
thorium,
titanium,
tungsten,
vanadium,
yttrium,
zinc,
zirconium.

Routine Spectrochemical Analysis of Aluminium and its Alloys.

§ 164. As will be seen later, there is general agreement that in aluminium alloys trouble is caused by microscopic heterogeneity, namely that which is associated with the crystalline structure.

The first method given *below* for the analysis of aluminium alloys is simple, straightforward, and practical. It has been carefully tested in my laboratory, and found to give reliable results if both standard specimens and those to be analysed have been prepared in substantially the same way.

Frommer, Gauthier, Handforth, and others (§§ 168, 168. 1) examine the specimens in the metallic form, taking careful precautions to ensure similarity in the behaviour of the electrodes, and special care in casting the specimens to avoid the formation of a coarse crystalline structure.

Bauer (§ 169) was so impressed with the likelihood of errors arising from this cause that he abandoned the use of the solid metal entirely, and used solutions of the metals to be analysed.

One may conclude that in the analysis of aluminium alloys it is of prime importance that the specimens to be tested should be prepared with care in the ways mentioned later, and that the standard specimens from which the graphs are obtained should be prepared in the same way.

Recommended Routine for Analysis of Aluminium Alloys.

§ 165. I propose first to give the procedure which has been adopted in my laboratory after consideration of most of those recommended in the literature. This procedure is recommended for the routine examination of such aluminium alloys as those specified in Table X. The procedure is identical for all the alloys in the table except L. 33, silicon and aluminium ; in this the most suitable silicon line, 2516 A., is so much stronger than the lines recommended for the other impurities that it requires a different length of exposure.

Spectrograph.—Medium quartz spectrograph.

Spark Circuit.—The investigations of Frommer (1939), Moritz (1939), and others, which are referred to later, seem to show that no better result is obtained by any published method of excitation than that given by the simple condensed spark (§ 87). The description of this may be found in Twyman and Hitchen (1931*a*), although it was in use many years before that.

TABLE X.—SPECIFICATIONS OF ALUMINIUM ALLOYS.

5 L.1.—“ Duralumin ” used for aluminium-alloy bars, extruded sections, and forgings.

B.S. Specification	Copper	3·5 to 4·5 per cent.
	Manganese	0·4 to 0·7 „
	Magnesium	0·4 to 0·7 „
	Silicon	Not more than 0·7 per cent.
	Iron	„ „ 0·7 „
	Titanium	„ „ 0·3 „
	Aluminium	The remainder.

The following are corresponding specifications ruling in U.S.A. and Germany :

A.S.T.M. B 89-36 T (1936)	Copper	3·5 to 4·5 per cent.
	Magnesium	0·2 to 0·75 „
	Manganese	0·4 to 1·0 „
	Aluminium	Minimum 92·0 „
Alcoa 14 S	Copper	4·4 per cent.
	Manganese	0·75 „
	Magnesium	0·35 „
	Silicon	0·8 „
DIN 1713 G Al-Cu-Mg (*DIN Taschenbuch,* p. 120)	Copper	3·5 to 5·5 per cent.
	Magnesium	0·2 to 2·0 „
	Silicon	0·2 to 1·5 „
	Manganese	0·1 to 1·5 „
	Aluminium	The remainder.

2 L.24 “ Y.”—Aluminium alloy used for castings.

B.S. Specification	Copper	3·5 to 4·5 per cent.
	Nickel	1·8 to 2·3 „
	Magnesium	1·2 to 1·7 „
	Aluminium	The remainder.

The following impurities may be present :

Silicon	Not more than 0·60 per cent.
Iron	„ „ 0·60 „
(Si + Fe	„ „ 1·0 „)
Lead	„ „ 0·05 „
Tin *plus* zinc, a total of	„ „ 0·10 „
Titanium	„ „ 0·20 „

The following are corresponding specifications ruling in U.S.A. and Germany :

SAE Spec. No. 39 (Type 2 alloy)	Copper	3·5 to 4·5 per cent.
	Nickel	1·7 to 2·3 „
	Magnesium	1·2 to 1·8 „
	Iron	Not more than 1·0 per cent.
	Silicon	„ „ 0·7 „
	Other impurities	„ „ 0·3 per cent.
	Aluminium	The remainder.
Alcoa 142	Copper	4 per cent.
	Nickel	2 „
	Magnesium	1·5 „
DIN 1713 G Al-Cu-Ni	Copper	4 per cent.
	Nickel	2 „
	Magnesium	1·5 „
	Aluminium	The remainder.

TABLE X—*continued.*

L.33.—Silicon-Aluminium alloy used for castings.		
B.S. Specification	Silicon	10 to 13 per cent.
	Iron	Not more than 0·60 per cent.
	Manganese	,, ,, 0·50 ,,
	Zinc	,, ,, 0·10 ,
	Titanium	,, ,, 0·20 ,,
	Aluminium	The remainder.
	Certain modifying agents.	
The following are corresponding specifications ruling in U.S.A. and Germany :		
Alcoa 47	Silicon	12·5 per cent.
DIN 1713 G Al-Si	Silicon Aluminium	11 to 13·5 per cent. The remainder.
L.40.—"Hiduminium," aluminium alloy used for bars, extruded sections, and forgings.		
B.S. Specification	Copper	1·5 to 2·5 per cent.
	Nickel	0·5 to 1·5 ,,
	Magnesium	0·6 to 1·2 ,,
	Iron	0·8 to 1·5 ,,
	Titanium	Not more than 0·2 per cent.
	Silicon	,, ,, 0·1 ,,
	Aluminium	The remainder.

We find the best capacity and self-inductance to be 0·005 μf. and 0·25 mh. respectively. The sparking transformer is best run at the setting for 10 kv., and not at the full 15 kv.

Shape of Samples.—A number of suggestions as to the shape of the sample have been made (Mandelstam, Raiskij and Zehden, 1936, and others mentioned later), and trial of a number of these has led us to make the sparking surfaces of the samples 3 mm. in diameter with a flat surface. This surface may be filed, but if a large number of samples are to be analysed it is quicker and better to turn the surface on a bench lathe, running at high speed so as to avoid coarse grooves.

Dr. L. Frommer, of High Duty Alloys, Slough, points out that the practice of filing the surface of the samples should not be recommended without qualification. Broadly speaking, in the case of any alloy prone to spreading or smearing (such as most light alloys and all soft alloys) filing should be strongly discouraged, since it leads to contamination of the electrode surface by rubbing in foreign matter. Even if the utmost care is used by employing only clean files, and separate files for the different alloys, filings from one specimen remain in the teeth of the file and are then rubbed into the surface of the next specimen, so that the surface hit by the spark consists partly of the genuine material of the sample concerned and partly of particles of the sample previously filed.

In addition to that, in actual large-scale routine practice files will always be liable to be confused, and they are usually a source of uncontrollable contamination.

Condensing Lens.—A condensing lens forming an image of the electrodes at the collimator lens of the spectrograph (§ 54, ii) should be employed, thus using light from all parts of the source.

Standard Conditions of Exposure :

Spark gap .	4 mm.
Slit width .	0·025 mm.
Plate . .	Ilford " Ordinary."
Prespark .	30 sec.
Exposure .	40 sec.
Development .	2½ min. in normal-concentration standard gaslight M.Q. developer at 20° C. (68° F.).
Fixing . .	2 lb. of hyposulphite of soda, 2 oz. of potassium metabisulphite, 2000 ml. of water.

Line Pairs to be measured on Microphotometer.—For determination of

Magnesium,	0·4 to 1·1	per cent.,	Al 2652 Mg 2780.
Silicon,	0·3 to 0·6	,,	Al 2652 Si 2516.
Manganese,	0·45 to 0·65	,,	Al 2652 Mn 2939.
Iron,	0·4 to 0·7	,,	Al 2322 Fe 2395.
Copper,	3·8 to 4·6	,,	Al 2322 Cu 2247.

Graphs.—These are prepared, as described in Chapter IV, from standard specimens of carefully ascertained composition (§§ 68 and 69).

Alternative Lines.—An experienced worker in this field has suggested that the following line pairs will give slightly more consistent results than the line pairs given *above* :

For the determination of	magnesium,	Al 3050 Mg 2791.
,, ,, ,, ,,	manganese,	Al 3050 Mn 2949.
,, ,, ,, ,,	iron,	Al 2367 Fe 2395.
,, ,, ,, ,,	copper,	Al 2367 Cu 2247.

§ 166. Accuracy.—Spectrographic results show necessarily a certain amount of scatter (approximately following the Gauss law), so that, while the average error of a large number of measurements is moderate, in a certain percentage of cases rather considerable errors must be expected.

I am indebted to Dr. L. Frommer for Tables XI and XIA, which show the average deviation between chemical and spectrochemical analysis, and the mean intrinsic errors of spectrochemical analysis for iron, silicon, and magnesium, respectively, in various aluminium alloys ; these errors have been calculated from large numbers of mass experiments carried out by his laboratory in connection with large-scale routine application. From these tables it will be seen that the average error in most cases is between 3 and 4·5 per cent. of the content analysed. This means that, according to the Gauss law, at least 4 per cent. of the measurements taken must contain errors of more than double the mean error, *i.e.* of more than 6 to 9 per cent. of the content analysed.

TABLE XI.—AVERAGE DEVIATION BETWEEN CHEMICAL AND SPECTROCHEMICAL ANALYSIS.

Element.	Alloy.	Average Content, per cent.	Average Deviation in Percentage of Content.	Average Deviation in Percentage of Total Weight.
Iron . .	R.R.59	1·1	3·5	0·038
	R.R.56	0·9	4·3	0·039
Silicon . .	R.R.59	0·85	4·4	0·037
	R.R.56	0·90	4·5	0·041
	Dural.	0·60	4·8	0·029
Magnesium .	R.R.59	1·55	3·3	0·051
	R.R.56	0·90	5·6	0·050

TABLE XIA.—MEAN INTRINSIC ERROR OF SPECTROCHEMICAL ANALYSIS CALCULATED ACCORDING TO GAUSS LAW FROM LARGE NUMBER OF EXPOSURES.

Element.	Alloy.	Average Content, per cent.	Mean Deviation in Percentage of Content.	Mean Deviation in Percentage of Total Weight.
Iron . .	R.R.59	1·1	3·0	0·033
	Dural.	0·7	2·9	0·020
Silicon . .	R.R.56	0·90	3·4	0·031
	Dural.	0·60	4·4	0·027
Magnesium .	R.R.59	1·55	3·8	0·059
	R.R.56	0·90	2·9	0·026
	Dural.	0·60	4·1	0·025

Evolution of the Modern Technique of Analysing Aluminium.

§ 167. The following abstracts are selected as showing the development of methods—all the papers mentioned have points of interest.

The Stepped Sector.—Schleicher and Clermont (1931) used a rotating *stepped* logarithmic sector, this having the advantage that it is free from the uncertainty in determining the ends of the lines which is associated with the original logarithmic sector of Scheibe and Neuhäusser. The above authors use auxiliary metals as in the substitution (or auxiliary-spectrum) method of Schweitzer (§ 119). The most informative aspect of the paper is the inclusion of lists of many homologous line pairs suitable for semi-quantitative determinations of the constituents in question.

Gerlach and Riedl (1933) made a survey of the purity of commercial aluminium which supplemented the English work on the subject.

A paper by Smith (1935) deals with the investigation of the usual impurities in commercial aluminium by the means described in the book by the same author (1933). Smith's paper deals principally with the analysis of unalloyed aluminium. Quantitative estimations, sufficiently accurate for control of the purity of aluminium, are made by the use of an auxiliary spectrum. Both arc and spark spectra are considered, and the spark preferred for routine analyses. The sensitiveness with the spark is adequate for the purpose in view, since the following proportions of the impurities can be detected :

Element.	Proportion, per cent.	
Copper .	Probably somewhat less than	0·001
Iron .	Approximately	0·004
Manganese .	Approximately	0·001
Silicon .	Somewhat less than	0·005
Titanium .	Approximately	0·001

Where the smallest traces of impurities are sought, in particular gallium, lead, and manganese, the arc method is required.

The auxiliary-spectrum method was the same as employed by Smith (1933) in previous work on the analysis of copper and lead. For the analysis of aluminium he used as the auxiliary an alloy of aluminium containing 1 per cent. of nickel. The nickel lines appearing were very suitable as standards of intensity for the impurity lines in the spectra of aluminium samples. Moreover, the spectra of the samples and of the auxiliary alloy were photographed under the same conditions. Tables are given for the approximate quantitative determinations of the above-mentioned impurities using the usual conventional notation: <, =, and >, meaning that the strength of the impurity line is less than, equal to, or greater than the strength of the nickel line selected for comparison.

Triché (1937), working for the French Air Ministry, dealt with the estimation of magnesium and silicon in a novel way, and van Someren published a paper (1934) on the estimation of copper, zinc, iron, silicon, manganese, magnesium, nickel, tin, and cadmium.

The Internal-standard Method of Spectrographic Analysis, as applied to "Pure" Aluminium, and Magnesium Alloys (Whalley, 1937).—In this paper Gerlach's internal-standard method is applied to the determination of iron and silicon in commercial "pure" aluminium, while a modification of the method is described for the analysis of magnesium alloys in which a composite spectrum is obtained from the spark struck between the magnesium alloy and nickel, the nickel providing lines for comparison which are not available in the magnesium spectrum.

§ 168. Various Modern Techniques using the Microphotometer.—In the discussion of a paper by Twyman on "The Industrial Application of Spectrography in the Non-ferrous Metallurgical Industry," Frommer, Gauthier, and Handforth give particulars of the respective techniques employed in their laboratories using the microphotometer (Twyman, 1939).

Gauthier * describes the testing of :

(*a*) Various grades of aluminium.

(*b*) Aluminium alloys with 1·25 per cent. of manganese, both with and without 1·5 per cent. of magnesium.

(*c*) Duralumin, for all constituents except copper, the only suitable lines for which, 3247 and 3274 A., do not give satisfactory results when the copper is between 3·5 and 8 per cent.

(*d*) Alpax or Silumin (for manganese and magnesium, but not for silicon).

(*e*) Magnesium-aluminium alloys with up to 5 per cent. of alloying element (his experience with richer alloys had not yet been sufficient to guarantee an accuracy of ± 3 per cent.).

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* Gaston G. Gauthier, Head of the Research Laboratories, Compagnie des Produits Chimiques et Électrométallurgiques Alais, Froges et Camargue, Chambéry, France.

Spectrographic analyses were made by the microphotometer. Two specimens were taken as standards, and 4 exposures of each made on the same plate, followed by 40 exposures of a third sample which was treated as an "unknown" alloy. Three plates were prepared in this way, and the manganese, iron, silicon, etc. contents of the "unknown" obtained by comparison of the appropriate lines with those of the standards; from these results the Gauss curve of errors was plotted. If the errors exceeded ± 3 per cent. of the values found by chemical analysis, their source was investigated. In the case of iron determinations the results were found to be consistently high, and this was traced to contamination by the tools; washing with 50 per cent. nitric acid before sparking eliminated this source of error.

Gauthier prefers a test-piece with a flat rectangular end 8 mm. long × 1·5 mm. wide prepared from a piece cast in the way he describes in the reference (p. 395). He has satisfied himself by X-ray examination that specimens prepared in this way have a sufficiently small amount of heterogeneity for it to be negligible.

Frommer * confines his remarks principally to the estimation of magnesium in Hiduminium R.R. alloys, of which his laboratory handles about 40 or 50 samples per day, besides many other light-alloy specimens. The specimens were prepared from the melt to be analysed by pouring a small portion of the melt into a chill mould of such shape as to provide 8 rods of 6 mm. diameter, which were used as the electrodes. Standard melts were prepared in precisely the same way, the standard castings being chemically analysed. Comparison between the results obtained with the ordinary condensed spark and with the Feussner generator showed no superiority of the Feussner spark as regards the estimation of magnesium in aluminium alloys. Frommer points out, however, that the spectrograms show denser lines when obtained with the Feussner spark with its rotating interrupter than when the interrupter is not used, a result which is obtained very easily by the tandem spark (Barratt, Triché, and Zehden).

Frommer also failed to find any improvement in the accuracy of the analysis by irradiating the spark gap with ultra-violet light, as has been advocated in some quarters. In fact, as far as his

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* Leopold Frommer, Research Metallurgist, High Duty Alloys, Ltd., Slough, Bucks., and Associated Companies.

results showed any difference at all, they were slightly worse when so obtained.

In discussing the question of presparking, Frommer gives it as his experience that the long presparking periods which have been recommended by some workers are not advantageous. He suggests that these long periods have been arrived at by paying too much consideration to the obtaining of a stable condition, as indicated by the relative intensities of the pairs of lines which are measured. In practice, what is important, however, is not whether the line-intensity ratio remains stable, but how accurately it is reproduced at a given interval of the running time of the spark in a number of exposures of specimens of identical composition, and how far its value differs for two specimens whose contents of the element to be analysed differ by a given amount. On the first point depends the consistency and on the second the sensitivity (slope of calibration curve) of the method. Frommer says that the estimation of magnesium in Hiduminium R.R. 59 offers a good example of this. The line-intensity ratio Al 2816 : Mg 2791 falls rather steeply during the first three minutes of sparking, and then tends to assume a constant value. However, with short presparking periods (*e.g.* 30 sec.) it reproduces very well, and gives a sensitive calibration curve ; therefore satisfactory results are obtained in spite of the variability of the line-intensity ratio with time, thus allowing speedy working.

The experience of my laboratory confirms this opinion.

J. R. Handforth stated that in the analysis of aluminium alloys his laboratory presparks for 20 sec. and exposes for 40 sec.

§ 168. 1. Moritz (1939), after eight years' experience in the application of spectrochemical analysis to the heavy metals, was encouraged to apply it also to light metals. In common with others working in this field he met at first with unexpected difficulties, but reached finally the practical result that the entire light-metal production of the works could be controlled with a method of analysis of satisfactory accuracy for works control and with great speed.

He considers three conditions of prime importance :

(1) Form and mode of preparation of electrodes.

(2) The technique must be practical and give reproducible results.

(3) The suitability of the lines used for quantitative determinations must be carefully tested.

Moritz draws attention to the necessity of preparing the electrodes in such a way that they will be so homogeneous that the results of analysis on the small surfaces attacked by the spark will give a result corresponding to the composition of the test-piece.

The well known difficulties attending the casting of homogeneous aluminium alloys are surmounted by casting the electrodes in a copper or iron chill mould, important considerations here being that the molten metal should be thoroughly hot, the pouring carried out rapidly, and the electrodes rapidly chilled. Moritz uses a microphotometer, calibrating the plate with a stepped wedge in front of the slit.

With regard to the influence of the form of the electrodes, he refers to a paper by Seith and Beerwald (1938). These investigators were experimenting on the analysis of magnesium alloys, using nickel as one of the electrodes. They found that when the ends of the nickel electrode had a diameter of 1 mm. the intensity of the nickel lines was about 2½ times as great as if the diameter of that electrode were 5 mm. Further, the variation of the intensity of the aluminium lines with increased concentration was considerably increased with the 5-mm. diameter nickel electrodes.

Moritz adopted a form of electrode with a diameter of 6 mm. The end surface is rounded on the edges, but in the middle it is turned flat 3 mm. in diameter. By using a special tool for this purpose, the same shape is always obtained without any difficulties.

Impressed by the opinion of Gerlach (1938) to the effect that the Feussner spark suffices for experiments with all metallic electrodes, Moritz worked with it for some months, but on account of the unsatisfactory results he reverted to the simple condensed spark. Later, further advice relative to its use having been brought to his knowledge, he tried the Feussner spark once more, but still without being able to find any advantage over the simple resonant circuit. This conclusion refers to experiments with aluminium and aluminium alloys ; with other metals such good results were obtained with the ordinary resonant spark that no comparison was made with the Feussner.

Moritz originally held rigidly to the principle of comparing, for purposes of quantitative analysis, only arc lines with arc lines and spark lines with spark lines. He says : "In the beginning we strictly observed the principle to compare arc lines of *Z* only with arc lines of *G* and spark lines of *Z* only with spark lines of *G* for carrying out the analyses. As to arc lines of *G*, the only one suitable for working without stepped filter appeared to be the line Al 2652·4, which, however, apart from its great distance from the *Z* line used, in systematic experiments was found to be unsuitable. We therefore abandoned that rule and tried lines in suitable positions without considering their atomic energy states. In doing so it appeared that if our routine analyses were always carried out under exactly the same sparking conditions, the atomic state of the line was of no importance provided the line was otherwise suitable."

§ 169. Bauer (1940) says that in the determination of manganese and magnesium in aluminium alloys by the customary methods results obtained in his laboratory were not exact enough (implying by " exact " that the errors should not be greater than ± 5 per cent.). Using metallic specimens, he found, from the evaluation of about 320 spectrochemical and chemical determinations, that the difference between the two was outside the 5 per cent. limit for 22·7 per cent. of the manganese and 34·5 per cent. of the magnesium determinations. He attributes these discrepancies to irregular distribution of the constituents in the electrodes. By specially careful casting of the electrodes and exact control of the casting temperature, chilling speed, and so forth, it may be that these errors could be avoided. " But it would still," he says, " not be possible to analyse any except cast specimens with the desired accuracy, since one could not be assured that in machined specimens the heat-treatment and grain-size of specimen would be identical with those of the standard electrodes." (*Translation.*) He considers that the testing of large quantities of aluminium alloys cannot be carried out with the necessary accuracy using solid electrodes, since the results are correct only for the place which is sparked and do not give an average value.

Impressed with these considerations Bauer goes on to consider the proposals put forward from various quarters to carry out spectrochemical analysis with solutions of the materials. The use of solutions has the advantage that the constituents are uniformly distributed but the disadvantage that it is not easy to ensure reproducible conditions for bringing the solution into the light-source (flame, spark, or arc). A simple way of obtaining a spectrum from solutions is to steep spectroscopically pure carbons therein and to spark these after drying in a drying cupboard (§ 131). Other ways are described in § 91.

Scheibe and Rivas (1936) endeavoured to combine the advantages of both these ways by dissolving the specimen to be analysed, introducing it into a heated carbon electrode, and then sparking the carbon with the dried-in coating, and this is the method adopted by Bauer following the results of Rivas (1937).

One gram of the specimen in the form of chips was dissolved in 25 ml. of 50 per cent. hydrobromic acid, the bromine boiled off, and the solution evaporated to the thickness of syrup, then dissolved in water, washed into a 50-ml. measuring flask, and diluted to the mark. From this solution about 0·003 ml. was put on to each carbon. Contrary to Rivas's procedure Bauer preferred weak solutions, since the concentrations given by Rivas were taken up by the carbon too slowly. Measurements were made with the microphotometer in the usual way.

From a synthetically prepared solution which contained 1 per cent. of manganese, 1 per cent. of magnesium, and the remainder aluminium, specimens were sparked many times in the above manner, and the result was plotted as a graph. It was found that the limit of error ± 5 per cent. was never exceeded. The same technique was used to determine the manganese and magnesium content (about 1 per cent.) in aluminium-magnesium-silicon alloys. In this series of experiments only 2·4 per cent. of the manganese and 6·9 per cent. of the magnesium values lay outside the permitted tolerance. The experiments were then extended to cover the copper-containing aluminium alloys. With these a further advantage of the solution method appeared. The standard curves for manganese and magnesium determinations were the same for both the copper-containing and the copper-free alloys. From this it follows that all the aluminium alloys can be determined on one plate with only three standard solutions, an advantage which, Bauer says, is not possible with solid electrodes. Silicon determinations are not possible with this technique, since in the solution silicon forms a silica precipitate.

Bauer used a Feussner sparking apparatus, but the interrupter was cut out, so that the apparatus became in effect an ordinary oscillating spark.

§ 170. Determination of Lithium in Aluminium Alloys.— Sukhenko (1939) determined lithium in aluminium alloys using the lines Li 6708·07 and Fe 6400·00 A.

A condensed spark between the aluminium-alloy specimen and an Armco iron electrode was used as the light-source, the potential being derived from a 0·5-kv. transformer, with a primary current of 4 amp. at 95 v., the circuit including a capacity of 0·01 μf.

The spark gap was 3 mm. Panchromatic plates and an exposure of 15 sec. were used. The intensity of the lines was determined by the method of photometric interpolation.

Experiments with known aluminium alloys showed that the pair of lines selected was sufficiently homologous. The presparking time employed was 30 sec. Results obtained for specimens containing 0·04 to 0·07 per cent. of lithium showed that the probable error of a single determination did not exceed ± 6 per cent.

§ 171. **Visual Spectrometric Analysis.**—Scheibe and Schöntag (1936) deal with the rapid determination in aluminium of sodium, copper, magnesium, and silicon in the following proportions :

	Per cent.
Silicon	up to 2
Sodium	up to 0·01
Copper	up to 10
Magnesium	up to 1·8

Iron was also determined. The authors used the visual spectrophotometer described by Scheibe and Limmer (1932).

The paucity of lines in the visible part of the aluminium spectrum in the neighbourhood of the lines of silicon, magnesium, sodium, copper, and iron is overcome by using air lines, which, with the apparatus described, they find sufficiently constant relative to the lines of the aluminium and all the metals to be determined.

Use is also made of another device : only the lower electrode is of the aluminium alloy under test, while the upper one is of copper. Naturally the entire radiation from the spark must be utilized. (The paper should be consulted by anyone interested in applying the Steeloscope or other visual type of instrument to the rapid analysis of aluminium alloys.)

§ 171. 1. **Beryllium in Alumina Mixtures and in Magnesium Alloys.**—Fesefeldt (1928) describes in this paper the detection of beryllium in the arc, and determines the sensitiveness of beryllium detection in Al_2O_3-BeO mixtures, and the influence on that sensitiveness of foreign substances such as sodium carbonate, lime, iron oxide, and silica (see also § 216. 1).

§ 172. **Other Investigations.**—The following papers also contain matter of interest :

Effect of Titanium (*Schleicher and Clermont*, 1931).—Constituents determined : titanium from 0·005 to 0·29 per cent. ; silicon from

0·09 to 0·14 per cent.; iron from 0·11 to 0·16 per cent. Excitation: spark. For the titanium estimation these authors find it necessary to add gold to give an internal standard, since there are no suitable aluminium-titanium line pairs. Aluminium containing titanium shows an effect of great importance: if a test-piece is broken and a number of exposures taken using the broken surface, the spectra differ; the aluminium lines are strong at first, and become gradually weak until they reach a uniform intensity. This is not imperfect distribution of the titanium, but is what Gerlach and Schweitzer observed in gold specimens containing a small admixture of lead, and they call it the *Korngrenzenschicht* or "grain-boundary" effect. Lists of homologous line pairs are given.

Duralumin (*Baschulin*, 1934-5).—Constituents: magnesium and manganese from 0·3 to 0·7 per cent.; silicon and iron from 0·1 to 0·7 per cent. Excitation: spark. Quantitative method: homologous line pairs. The homologous line pairs and fixation pairs are given.

Smith (1935).—Constituents: copper, iron, silicon, titanium, manganese, gallium, and lead. Excitation: arc and spark. Preparation of substance: cast into rods. Quantitative method: comparison samples and auxiliary-spectrum method. For the routine analysis of aluminium samples one standard alloy of aluminium with 1 per cent. of nickel suffices for the estimation of the above impurities by the auxiliary-spectrum method. The method consists in superimposing by photography the spectra of the specimen under test and of a standard specimen, thus providing what amounts to an internal standard. Details of suitable lines for the various methods are given.

Van Someren (1934).—Constituents: copper, zinc, iron, silicon, manganese, magnesium, nickel, tin, and cadmium. Excitation: spark. Preparation of substance: cold-rolled to strip, from which electrodes were cut. Quantitative method: homologous line pairs. The paper aims at enabling users of a spectrograph to find the approximate composition of any unknown aluminium alloy so that the alloy can be identified. Twelve commercial alloys and fifty synthetic alloys were used to obtain the results recorded in the paper. Tables give percentages at which the impurity lines equal selected lines of aluminium.

Koch (1936).—Constituent: magnesium. Excitation: spark of 15,000 v., 0·02-μf. condenser, 60 cycles, 2-mm. spark gap, 10-sec. exposure; also arc between sample and upper electrode of graphite, 2·5 amp., 70 v. across gap (220-v. supply), 30-sec. exposure. For the arc samples were sawn from ingots. Quantitative method: densities measured on recording microphotometer; measurements were made on dark line and clear background, but no correction was made for background; the logarithm of the percentage content was plotted against the density difference magnesium-aluminium. The author concludes that a 10 per cent. accuracy can be obtained from one reading in the magnesium-content range from 0·1 to 4·0 per cent. Two spark lines give better results than one spark line against an arc line.

Aluminium and Silumin (*Sukhenko*, 1937).—Constituents: magnesium, silicon, iron, and copper. Excitation: spark. Quantitative method: homologous pairs compared by visual examination with magnifying glass. The paper gives tables of concentrations of the constituent at which one of its spectrum lines is equal in intensity to a line of the basis metal. Accuracy of determination claimed in aluminium: silicon to 3 per cent., and iron to 1·5 per cent.; in silumin: magnesium to 5 per cent., and iron to 11 per cent. The very large error in the case of the iron determination in silumin is attributed to an error in the chemical analysis. (The paper is in Russian.)

CADMIUM.

§ 173. **High-purity Cadmium.**—Lamb (1935) points out that the cadmium used for electroplating requires to be of very high purity. Even 0·001 per cent. of thallium is objectionable in electroplating, causing blistering. The question of an easy method of analysis is of considerable importance, since in 1934 no less than 2,777,384 lb. of cadmium was produced in the United States, two-thirds of it being used for the electroplating of small articles.

The producers of cadmium have gradually increased the purity of their product to 99·99 per cent.

The impurities: zinc, lead, iron, copper, nickel, and thallium were determined by Lamb (*loc. cit.*) using an arc between graphite electrodes impregnated with an acid solution of the metal, following the procedure described by Nitchie and Standen (1932). Estimation was made by visual comparison with standard synthesized samples of known composition. Full particulars are given in the reference.

The method was also applied by Lamb to the analysis of cadmium-base alloys and cadmium compounds.

In the high-grade cadmium produced by the National Smelting Company, Avonmouth, the impurities: zinc, lead, and thallium are determined by the use of comparison standards.

§ 174. In preparing the supply which will be used as an illustration of high-purity cadmium (Hilger, 1935*b*), the refining was pushed to the limit, and the total impurities appear to be substantially less than one part in a million.

The metal was finally cast into rods 7 mm. in diameter and 15 cm. long.

The metal was analysed in the works, and after delivery submitted to spectrochemical examination. By reason of the exceptional purity, no chemical analysis was practicable, hence the whole analysis was conducted spectroscopically in the following manner:

(1) Pieces of the metal were mounted on very pure copper electrodes and examined by the arc method, using a medium quartz spectrograph with sphero-cylindrical quartz condenser. The current across the arc was 3·2 amp., and the voltage 35. Exposure: 60 sec.

(2) This was repeated using very pure silver electrodes, in search for copper. The voltage, current, and exposure were the same as in (1).

Each process was repeated, making four spectra in all.

The spectrograms revealed minute traces of three elements:

(*a*) *Bismuth.*—The *raie ultime* at 3067·732 A. appears as a faint line in three out of four spectra, but no other line is in evidence. The proportion present was determined by reference to a bismuth-in-zinc standard, and found to be less than 1 part in 1,000,000; probably not more than 1 in 5,000,000.

(*b*) *Lead.*—This was indicated by the 2614·20, 2802·01, and 3683·47-A. lines, all barely visible (but the 3683·47 line was not visible when silver electrodes were used). The 2833·06 and the 3639·57-A. lines were not in evidence. On reference to standards, the proportion present was found to be much less than 1 part in 1,000,000; probably not more than 1 in 5,000,000 to 10,000,000.

(*c*) *Copper.*—This was indicated by the 3247·550-A. line, and the proportion present estimated to be less than 1 part in 2,000,000.

Hence, the total metallic impurities do not exceed about 1 part in 1,000,000; therefore

Cadmium, by difference.—99·9999 per cent. less any non-metals present.

Elements specially sought in the above-described spectra with negative result :

aluminium,
antimony,
arsenic,
barium,
beryllium,
boron,
calcium,
chromium,
gallium,
germanium,
gold,
indium,
iron,
magnesium,
manganese,
molybdenum,
nickel,
potassium,
silicon,
silver,
sodium,[*]
strontium,
thallium,
tin,
titanium,
tungsten,
vanadium,
zinc.

From a knowledge of the details of the process of preparation, and other considerations, there is reason to assume the entire absence of *non-metals*, except possibly hydrogen or oxygen.

COPPER AND ITS ALLOYS.

Pure Copper.

§ 175. A batch of metal (Hilger, 1940*b*) which was specially refined for the purpose of spectroscopic research will afford an illustration of the examination of pure copper.

The metal was in the form of rods, 5 mm. in diameter and 17·5 cm. long. Each rod was pickled in acid, washed in distilled water, and dried under appropriate conditions to avoid surface contamination. Eight rods were taken at random from the parcel, and used a pair at a time to form an arc, which was photographed with a medium quartz spectrograph. The arc was struck from the main at 200 v. D.C. with a current of 5 amp. and 3·2 amp., the latter current being better for lead, tin, and antimony ; the exposure was 5 min., with the arc focussed on the slit. The lead and tin were determined spectrographically by indirect comparison with copper rods the contents of which had been established.

In the course of chemical tests, small precipitates were obtained which on spectrographing showed traces of silver, arsenic, bismuth, lead, and tin. Spectrographic estimations of the quantities so found by comparison with synthesized specimens were calculated back to the original metal, and are included in Table XII.

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[*] Except perhaps a minute trace due to surface contamination.

TABLE XII.—ANALYSIS OF PURE COPPER.

Element.	Remarks.	Lines in Evidence, A.
Antimony	Very slight trace.	2598·08 (in the 3·2-amp., 5-min. spectrum only).
Arsenic	Very slight trace.	...
Bismuth	Very slight trace.	...
Iron	0·0007 per cent.	3581·197 3570·102 2973·236 2973·137 2966·902 2599·405 2488·148 2485·277 2382·039
Lead	Less than 0·0001 per cent.	2833·06
Silver	Very slight trace.	...
Gold	Very slight trace.	...
Tin	Very slight trace.	3009·14 2863·32 2839·98
Oxygen	0·012 per cent.	...

Elements specially sought in the spectrograms of the rods described in Table XII, but not found, were

aluminium,
barium,
beryllium,
boron,
cadmium,
cæsium,
calcium,
chromium,
cobalt,
gallium,
germanium,
gold,
indium,
lanthanum,
lithium,
magnesium,
manganese,
molybdenum,
nickel,
palladium,
phosphorus,
platinum,
potassium,
scandium,
silicon,
sodium,
strontium,
tantalum,
tellurium,
thallium,
thorium,
titanium,
tungsten,
vanadium,
zinc,
zirconium.

In order to realize the full advantage of rods of such high purity, it is desirable to remove any surface contamination by a brief pickling in dilute nitric acid followed by washing in distilled water.

Impurities in Copper.

§ 176. Milbourn (1934) describes a convenient method for the detection and estimation of small quantities of bismuth, arsenic, lead, iron, nickel, silver, antimony, and tin by the globule method of van Someren. Working on small samples of brass, van Someren (Brownsdon and van Someren, 1931) had observed that increased sensitiveness to a number of impurities occurred when the specimen was in the form of a globule between the graphite electrodes of an arc. This is the method used by Milbourn. It was also used by Hill and Luckey (1919), Hitchen (1933), and Smith (1933).

Employing an arc 4 mm. long carrying a current of 5 amp., Milbourn used a pure copper rod as one electrode (the positive one), while the lower and negative electrode consisted of a graphite rod, in a shallow cup in the end of which is placed a small portion, 0·02 to 0·05 g., of the sample to be examined. When the arc is run, the specimen melts forming a globule, and it is found that considerably greater sensitiveness is obtained in this way than if solid electrodes of the specimen to be tested are used. This increased sensitiveness is obtained with bismuth, arsenic, lead, nickel, antimony, and tin. The sensitivity to iron and silver is not much increased.

If the sample adheres to the copper rod, or if the arc tends to pass to the graphite, then the electrodes should be manipulated until a suitable, steady arc is obtained. The cup in the end of the graphite rod should be just sufficiently deep to keep the molten globule in place.

The copper rod used contains the following small amounts of impurities, as estimated from tests in which a small portion of it was made the globule : lead, slight trace (Pb 2833·1 A. just visible) ; iron, about 0·001 per cent. ; nickel, about 0·0005 per cent. ; silver, about 0·002 per cent. ; and antimony, about 0·001 per cent. ; bismuth, arsenic, and tin are not detected.

Using other samples as globules and the above copper rod as anode, spectra are obtained in which lines due to such elements as lead, iron, and silver may be absent ; hence these small amounts of impurities are not affecting the spectrum.

Similarly, the graphite rod acts merely as a convenient conductor and easily cleaned support for the globule, and does not affect the character of the arc. Cyanogen bands and lines due to impurities in the graphite, such as vanadium, titanium, and silicon, do, however, appear when a graphite rod is used as anode instead of the copper rod. For this reason the copper rod is preferred.

The copper spectrum obtained from a globule arc is radically different from that given by a solid-electrode arc. The spark lines appearing near the poles in the latter are practically suppressed in the former, and many lines absent from or appearing only faintly in the solid-electrode arc occur with considerable intensity in the globule arc. The factors, such as temperature and electrical conditions in the arc, which favour the appearance of these lines also enhance most of the impurity lines. Many of the faint " background " lines are nearly absent from the globule arc ; this also assists in the observation of impurity lines.

Tables are given whereby approximate quantitative estimations can be made of the impurities mentioned, by the simple internal-standard method.

The author concludes that the globule method is well suited for the examination of relatively pure coppers. In testing arsenical coppers the estimation of the arsenic content may tend to be low owing to the rapid loss of arsenic in the globule, unless the precaution is taken of exposing the plate during the early stages of arcing. The author notes that the quantitative results given by this method with coppers de-oxidized with phosphorus are not reliable. The presence of even 0·04 per cent. of phosphorus in the globule will show a marked reduction in the volatilization of the copper globule as compared with that of copper free from phosphorus.

At I.C.I. Metals, Ltd., tellurium in copper has been detected by this method down to 0·001 per cent., and quantitative estimations have been made down to 0·01 per cent. Besides the most sensitive lines 2383 and 2386 A., at 0·01 per cent. 2259 and 2531 A. also appear. For selenium in copper the small quartz spectrograph is better, on account of the increased transparency to very short waves resulting from its smaller quartz optical system. The lines 2040 and 2063 A. were used to detect selenium in concentrations down to 0·005 per cent. If the medium quartz spectrograph is used the most sensitive line for selenium in the arc spectrum is at 2413·5 A.

§ 177. Method of Analysis at the British Non-ferrous Metals Research Association.—The standard method of analysis used in the B.N.F.M.R.A. laboratory is that of the 7-amp. globule arc, and Table XIII gives the estimated limits of detection of impurities by this method.

TABLE XIII.—IMPURITY LIMITS IN ANALYSIS OF COPPER (B.N.F.M.R.A.).

Element.	Limit, per cent	Element	Limit, per cent.
Antimony .	0 0002	Nickel . .	0 0001
Arsenic . .	0 002	Tin . .	0 0005
Bismuth . .	0 0001	Zinc .	0 001
Cobalt . .	0 0001	Manganese .	Not known with certainty, but probably lying between 0 001 and 0 0001
Iron .	0 0002		
Lead .	0 0002		

§ 178. *Breckpot and Mevis* (1934, 1935*a*, 1935*b*) should be consulted on the determination of

aluminium,
antimony,
arsenic,
barium,
bismuth,
boron,
cadmium,
calcium,
chromium,
cobalt,
germanium,
gold,
indium,
lead,
lithium,
magnesium,
manganese,
molybdenum,
nickel,
phosphorus,
potassium,
silicon,
silver,
sodium,
strontium,
tellurium,
thallium,
tin,
titanium,
vanadium,
zinc.

They work with copper-oxide samples, a procedure for which they claim advantages.

A paper by R. Breckpot (1935*a*) describes the determination of traces of bismuth, arsenic, antimony, tin, and lead in electrolytic copper, by concentration of the impurities by coprecipitation with ferric hydroxide, substitution of a copper base for the iron base, and subsequent spectrographic analysis.

Schleicher and Wunderlich (1939) observe that the presence of dissolved oxygen affects the spectrographic determination of arsenic in copper. The disturbing effect can be eliminated by cathodic pretreatment of the electrodes and sparking in hydrogen. The possibility of determining oxygen in copper is also suggested, but this does not appear to have been fully worked out. The paper should be consulted by those interested in refining copper. A later paper (Wunderlich, 1939) deals particularly with the estimation of arsenic in copper.

The Analysis of Brasses and Bronzes.

§ 179. In the analysis of brasses and bronzes the spectrograph may generally be used for the determination of constituents not exceeding 5 per cent., but for constituents present in quantities exceeding 10 per cent. the spectrograph is not yet of practical utility.

For example, Mr. D. M. Smith, Chief Spectroscopist of the British Non-ferrous Metals Research Association, tells me that the analysis of 76/22/2 aluminium-brass would be efficiently carried out in the following manner :

Copper . . .	By chemical analysis.
Aluminium . .	Spectrographically, using the microphotometer.
Impurities . .	Spectrographically, using a method of the internal-standard type.
Zinc . . .	By difference.

In general, he would recommend that for brasses the copper should be determined chemically, the impurities and added constituents not exceeding 2 or 3 per cent. by spectrographic analysis, and the zinc by difference.

In the chemical analysis of bronzes the copper and the alloying constituents would be determined by the standard method. The question of applying spectrographic methods depends on the accuracy required and the time taken in analysis.

I may mention here that in my laboratory tin in bronzes has been successfully estimated in proportions up to 7 per cent. with an accuracy of within 5 per cent.

§ 180. Details of some quantitative routines for the spectrographic examination of brass by the simple internal-standard method are given by Brownsdon and van Someren (1931). They find that no advantage is to be gained in sensitivity by using the metal under test for both negative and positive electrodes, so that they use the sample only as negative electrode, thus saving time. Electrical conditions of the arc are controlled by having an ammeter in series with the arc, and a current of .5 amp. is used, the specimens being in the form of 6-mm. diameter rods, or (in practice) small cubical ingots or thick strips. For the positive electrode a 6-mm. diameter rod of pure copper is used. The authors prefer to work without a condensing lens, and use a small quartz spectrograph, which they find sufficient for the purposes of this particular type of examination.

The paper gives tables whereby a rapid approximate analysis can be obtained of

Lead	0·005	to	5·0	per cent.
Tin	0·005	to	1·3	,, ,,
Iron	0·005	to	1·2	,, ,,
Nickel	0·01	to	15·0	,, ,,
Aluminium	0·01	to	2·0	,, ,,
Manganese	0·01	to	1·6	,, ,,

§ 181. Using the internal-standard method (§§ 117 and 118), Barker (1939) employs an arc the lower electrode of which consists of the specimen under test, and this is made the negative electrode. The upper (positive) electrode is of pure copper, which Barker finds for most purposes to give as sensitive and reliable results as if both electrodes were made of the specimen under test, while saving time in the preparation of the specimens. The electrodes are in the form of rods of 5-mm. diameter, shaped at the ends to a cone of 80°. The author standardizes the conditions carefully according to the schedule given in Table XIV. With a large quartz spectrograph the maximum and minimum limits of estimation called for in the laboratory in question are given in Table XV. This table by no means indicates the limits within which spectrochemical

TABLE XIV.—STANDARD ANALYSIS CONDITIONS (BARKER).

(Arc gap: 4·0 mm.; slit width: 0·015 mm.)

Material.	Positive Electrode.	Current, amp.	Wave Band, Å.	Exposure, sec.
Copper	Copper	4·0	3000–5800	23
Brasses	,,	4·0	2800–4800	30
Bronzes	,,	4·0	2320–3000	45
Cupro-nickels	Copper	2·5	3000–5800	23
,,	,,	2·5	2800–4800	30
Monels	,,	2·5	2320–3000	45
Aluminium and alloys	Graphite	4·0	2800–4800	60
Globule on all metals	Copper or graphite	4·0	3000–5800	15
		4·0	2800–4800	20
		4·0	2320–3000	30
Iron	Iron	2·5	3000–5800	5
Steel	,,	2·5	2800–4800	7
,,	,,	2·5	2320–3000	10

TABLE XV.—RANGE OF WORK UNDER ABOVE CONDITIONS (TABLE XIV).

(Percentages.)

Alloy.	Pb.	Bi.	Sb.	As.	Fe.	Ni.	Ag.	Al.	Mn.	Sn.	Zn.	Cd.
Copper	0·005–0·20	0·001–0·007	0·003–0·03	0·01–0·05	0·005–0·20	0·005–0·16	0·005–0·02	0·005–0·20	0·01–0·05	0·005–0·05	0·01–0·10	0·005–0·02
Copper-nickel, 95/5	0·005–0·20	0·001–0·007	0·003–0·03	0·01–0·05	0·005–0·20	..	0·005–0·02	0·01–0·20	0·01–0·05	0·005–0·05	0·01–0·10	0·01–0·05
Copper-nickel, 70/30	0·005–0·20	0·001–0·007	0·003–0·03	0·01–0·05	0·005–0·20	..	0·005–0·02	0·01–0·20	0·01–0·75	0·005–0·05	0·01–0·10	0·01–0·05
Monel metal	0·005–0·20	0·001–0·007	0·003–0·03	0·01–0·05	0·01–0·40	..	0·005–0·02	0·01–0·20	0·01–0·75	0·005–0·05	0·01–0·10	0·01–0·05
Copper-zinc alloys (2–3 per cent. Zn)	0·005–0·20	0·001–0·007	0·003–0·03	0·01–0·05	0·01–0·20	0·005–0·20	0·005–0·02	0·01–0·20	0·003–0·03	0·005–0·05	..	0·01–0·05
Gun-metal and phosphor-bronze	0·005–0·15	0·002–0·015	0·005–0·04	0·01–0·05	0·01–0·20	0·01–0·16	0·005–0·02	0·005–0·05	0·005–0·05	..	0·01–0·20	0·005–0·02
Brasses	0·005–0·20	0·001–0·007	0·003–0·03	0·005–0·05	0·005–0·12	0·005–0·16	0·005–0·02	0·002–0·20	0·002–0·02	0·005–0·20	..	0·005–0·02
Lead alloys	Qualitative examination only.									0·01–0·60		0·01–0·20
Zinc, tin, nickel	Qualitative examination only.											
Aluminium and aluminium alloys	Qualitative examination only. Development work in connection with quantitative analysis now proceeding.											

analysis is applicable to the alloys mentioned; it merely covers the ranges of composition most suited to the author's work. It is known, however, that smaller and larger amounts of most of the elements mentioned can be estimated by spectrochemical methods. As in the testing of pure copper, the simple method of internal-standard comparison gives sufficient accuracy.

§ 182. Cadmium-Copper Alloys (Twyman, Zehden and Dreblow, 1940).—Cadmium-copper is an example of an alloy presenting peculiar difficulties in spectrochemical analysis. A series of investigations in my laboratory has shown that the ordinary methods of quantitative analysis of the cadmium using the micro-photometer yield results entirely consistent with careful chemical analyses up to something under 1 per cent., but that when the percentage of cadmium becomes 1 per cent. or over, the method becomes quite unreliable. There seems little doubt that this is connected with the structure of the alloy. It may be stated that perfectly reliable results may readily be obtained by dissolving the copper-cadmium and sparking it in the tube described in § 91 (Fig. 28).

GOLD.

High-purity Gold (Hilger, 1936).

§ 183. To illustrate the purity attainable and the ultimate impurities likely to be found in high-purity gold, the example may be cited of a specimen guaranteed by the refiners to have a purity of at least 99·999 per cent., the statement being added that there was no impurity except possibly a trace of silver. Thus the quantities of foreign elements are so small as to be outside the scope of ordinary chemical determination.

A bead of 50 or 60 mg. of the gold was placed on the lower of a pair of very pure copper electrodes, and a spectrogram taken. This was repeated with a second bead.

Two spectrograms were similarly taken with electrodes of very pure silver. The current in each case was 3·0 amp. and the voltage across the arc 37. The exposure was 60 sec.

The four portions of metal were first heated with hydrochloric acid, and then with nitric acid, in order to remove any adhering contamination. Such treatment of any portion to be used is desirable in order to have the metal in its high state of purity.

All four spectra revealed remarkably little impurity.

Impurities found were

Silver . .	Only a very slight trace, indicated by the lines 3382·88 and 3280·70 A.
Sodium . .	Minute trace, indicated by 5895·932 A.; probably due to surface contamination.
Tin . .	Minute trace barely indicated by 2839·99 A.; practically 0.
Zinc . .	Minute trace, indicated by 4722·164 A.; barely visible.

Elements sought in the above-described spectra with great care, but with negative result, were

bismuth,
copper,
germanium,
iridium,
iron,
lead,
osmium,
palladium,
platinum,
rhodium,
ruthenium.

Other elements also sought, but with negative result, were

aluminium,
antimony,
arsenic,
barium,
boron,
cadmium,
calcium,
cobalt,
lithium,
magnesium,
manganese,
molybdenum,
nickel,
niobium,
potassium,
silicon,
strontium,
thallium,
vanadium.

Lead is probably quite absent. The only lines appearing which might be due to this metal are 2833·06 and 2802·01 A., but these lines are confused by the faint gold lines, 2833·05 and 2802·20 A.

Each of the foreign lines is so feeble that the total impurity must amount in the aggregate to less than 0·001 per cent., as claimed by the refiners. The gold-assay figure is 99·9995 per cent. Au.

Application of the Quartz Spectrograph to the Assay of Gold and Silver at the Royal Mint, London.

§ **184.** The application of the spectroscope to the assay of gold and silver has been studied in the laboratory of the Royal Mint, London, for a number of years. The general conclusions are :

(1) The arc spectrum affords a very sensitive test for the detection of several probable impurities in fine gold.

(2) The spark spectrum is of relatively little value for this purpose.

(3) The spectroscope is less useful for the detection and estimation of small traces of gold in other metals and materials than established chemical or assay methods (Rose and Newman, *The Metallurgy of Gold*, pp. 6, 532).

The investigations described were made with a medium quartz spectrograph, in which the spectrum from 2100 to 7000 A. covers a length of nearly 8 in.

For the gold arc spectra the samples are usually in the form of sheet 1 mm. to 1·5 mm. thick, from which two poles are cut 5 mm. wide and 30 to 40 mm. long. Contamination with iron from the rolling and cutting is removed by scraping followed by boiling in hydrochloric acid ; the poles are then heated to redness in air for a few minutes, and examined for spots of ferric oxide under low magnification.

These poles are satisfactory with an arc of 2·5 amp. ; poles 1·5 mm. thick will stand 3 amp., and the arc is then steadier.

With the smaller current considerable difficulty is found in maintaining the arc for the period, usually 20 sec., necessary for the exposure. If the arc is struck when focussed on the slit, and especially if it is restruck several times during one exposure, the air bands are much increased, and may make the detection of some faint lines difficult. The best practice in this respect is to strike the arc in a position where its image is not quite focussed on the slit, and then to move it into the correct position.

The use of an inductive resistance, an ordinary cylindrical sliding rheostat, is of some value in keeping the arc in action.

Specimens of fine gold containing 1 part in 10,000 and 1 part in 100,000 of silver and copper were prepared by melting pure gold *in vacuo* with the required proportion of alloys of known composition. The spectra of these show the persistent lines of silver and copper quite strongly, those due to 1 part per 10,000 being approximately three times as strong as those from the samples containing 1 part in 100,000. It would appear that the relation of the strength of these lines to the proportion of the trace of metal is approximately exponential, and extrapolation on that basis to the region of 1 part per 1,000,000 may be justified.

The persistent lines of calcium and silicon show strongly with such small traces that no difference can be found by assay between samples of gold which do not show these lines and others in which they are strongly visible. No means appears available of introducing comparably small proportions of these elements, but the amounts present when the corresponding lines are faint or absent must be less than one part in a million.

The spark spectrum is considerably less sensitive: samples of fine gold containing less than 1 part per 10,000 of impurity showed no "foreign" lines in the spark spectra, although silver, copper, calcium, and silicon lines were quite strong in the arc spectra of the same material.

In the course of an investigation into the detection of gold and silver in organic tissues small known amounts of gold were absorbed in pieces of filter-paper 1 cm. square, which were then rolled into cylinders and used to obtain spark spectra. It was found necessary to use 0·05 mg. of gold to get definite gold lines in the spectra—an amount much more readily detectable by assay methods. With silver under the same conditions 0·005 mg. was sufficient to give quite definite silver lines. It was evident that even smaller amounts of silver could be definitely recognized in a spark spectrum, and that considerably smaller quantities of silver can be detected by this means than by any chemical or assay method.

For the detection of gold in silver even the arc spectrum did not prove very sensitive: the line 2428·1 A. was visible in one spectrum of fine silver in which 1 part of gold per 100,000 had been found by assay, but other spectra of the same metal failed to show any gold lines.

Other Published Work on Gold.

§185. *Meggers, Kiess and Stimson* (1922) applied the spectrographic method to the assay of gold, comparing the intensities of the lines of impurities with those of the same lines of spectrograms taken from standard specimens of known composition.

The subject was raised by the Assayer of the U.S. Mint, San Francisco, who asked the Bureau of Standards if it could furnish or develop for him more reliable or economical methods of analysing the gold which went into the national coinage and reserve. The most persistent impurities to get rid of in purifying gold are silver, copper, lead, iron, nickel, and platinum metals. In grading the gold product of electrolytic refineries the Mint often has to decide whether the total impurity present is 0·01 or 0·02 per cent. (999·9 or 999·8 fine in gold), and individual fire assays may show a full 1000 fine in gold. There are, the authors say, no strictly assaying methods for the determination of individual base metals in gold bullion and such chemical analysis must of necessity be done by wet methods, most carefully carried out on very large amounts of metal when only minute traces of the base metal are involved. At least 15 g. of bullion is required in a test for 0·01 per cent. of iron, and complete analysis by chemical methods is excluded on account of the prohibitive cost in time and materials. Such analyses, however, are quite practical by spectrographic methods, for which only a few milligrams of material and an hour of time are required. The world's gold currency is estimated to be nearly $10,000,000,000 in value. If it is assumed that assays upon which this value is based are unable to detect 0·01 per cent. of impurities, then $1,000,000 is base metal. With the help of a well chosen series of standards the authors found that even the simple visual comparison of the lines gave results of considerable accuracy.

Mankin (1936) examined the spectra of alloys of gold and silver, using a bead in the lower of the two carbon electrodes of an arc, and measuring the densities of photographed lines by means of the microphotometer.

Thin films of gold, such as, for instance, those sputtered on to glass, mica, or ceramic bodies, may be analysed by the spark in the manner described in §§ 88. 1 and 97.

§ 186. Spectroscopic Analytical Control of Precious Metals.—To avoid the distortion of the incandescent thin metal wire in Occhialini's method (1929), Pastore and Occhialini (1938) wind it into a spiral 3 mm. in diameter, and insert this at right-angles to the arc between two carbon poles. The length of the lines of the main constituent gives an idea of the quantity of alloying elements present without the need for determination of each element individually, and this result can be obtained very rapidly. For platinum, gold, and silver the diameter of the wire used was 0·025 to 0·05 cm., and the spectral lines used were 5301·05, 5230·3, and 5465·43 A. respectively. Examples of determinations are given.

§ 187. *Gerlach and Schweitzer* (1928*a* and 1928*b*) deal with the determination of lead in gold. Their paper is in four parts :

Part I deals with observations of a novel character which first of all seemed to permit little prospect of success in such analyses, but later shows how to avoid the sources of error.

Part II deals with the method of analysis adopted.

Part III describes the substitution method, which facilitates determinations of impurities in cases where these, either on account of small concentration or on any other grounds, show only one or a few suitable spectrum lines.

Part IV includes a method by which a lead content in heavy metals of considerably less than 0·001 per cent. can be determined.

It is worth while giving a rather full abstract of the first three parts of the paper :

Part I.—The sparking apparatus was a Klingelfuss transformer with rotating mercury break. Capacity : from 0·003 to 0·01 μf. ; inductance : approximately 0·1 mh. In the first experiments to determine the effect of successive sparking (*Abfunk*, " presparking," or "spark-out" effect) in a specimen of gold containing 1 per cent. of lead, the electrodes were made with points sharpened with a knife, and a number of exposures each of 15 sec. were taken one after another. The intensity of the lead lines was found to become successively less, until it arrived at a steady value. A specimen containing only 0·2 per cent. of lead showed the same phenomenon. The final intensity of the 1 per cent. specimen was considerably greater than that of the 0·2 per cent. Fig. 42, reproduced from the reference, shows the falling off in the case of a number of specimens all of the same concentration. This occurs more rapidly with thin than with thick electrodes.

The curves show the results on specimens sharpened afresh each time, but sometimes interference was occasioned, when thick electrodes were used, by the spark suddenly springing to a fresh place, and the spectrogram showed then an increased intensity of the lead line (see " Funkensprung " in Fig. 42).

The same phenomenon is shown qualitatively with the copper which is present as an impurity, but in the case of silver the lines remain mostly constant. It was then tried whether the final intensity remained constant for a still longer succession of exposures, but the phenomenon then took on a contrary character. The intensity of the lead lines (not, however, those of the silver and copper lines) increased with time, then decreased again until it acquired once again a constant intensity. At the same time the band spectrum increased. This was attributed to the heating of the electrodes, which became incandescent. The use of the heating of the electrodes in the analysis of very small proportions of lead is dealt with in Part IV. As soon as the heating was avoided by a weaker discharge, the final intensity remained constant.

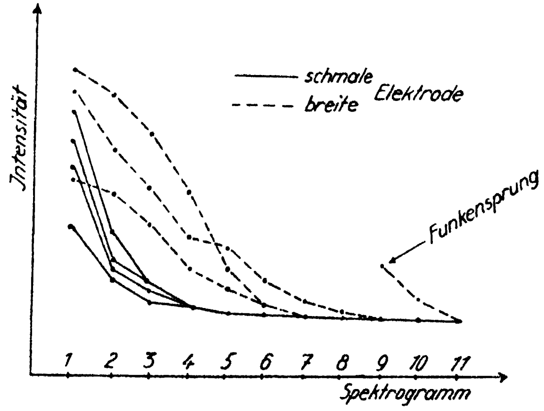

Fig. 42. – The *Abfunk* Effect for Lead in Gold.

To prove that the increase and subsequent decrease of the lead intensity was caused by the strong heating, the surface of the electrodes of a specimen of gold containing 0·8 per cent. of lead was melted with an oxy-hydrogen flame to form a rounded end. It was then found almost impossible to get a spark. The electrodes had to be approached to about 1 mm., as opposed to the ordinary 5 to 10 mm., and then the spark was only very feeble in illumination. Still, a spectrum could be taken, and it showed principally lead lines with very strong copper. After about 20 sec. the spark would pass with a greater distance between the electrodes, and then the intensity of the lead considerably decreased and corresponded to only about 0·2 per cent. of lead instead of 0·8 per cent. Further, the intensity of the copper lines was considerably smaller than in the unmelted test-piece, while on the other hand the intensity of the silver lines remained completely uninfluenced by the process. After cutting away the melted end, the specimen showed again the usual phenomena, giving a final intensity corresponding to the 0·8 per cent. of lead.

The explanation may be taken to be as follows :

On melting in the oxy-hydrogen flame the lead is oxidized, and forms a thin skin of very high dielectric strength. The spectrum first shows almost solely the metallic constituents of the skin. If this is damaged by erosion caused on the surface by heating through the play of the spark, the gold, with its small proportion of lead and copper, comes into operation, while the silver, which does not easily oxidize, remains practically unaltered.

The high initial intensity is dealt with by presparking every freshly pointed electrode for one to two minutes before the first exposure.

Numerous experiments were made in which the discharge took place in other gases than air to avoid oxidation, but in hydrogen, nitrogen, and argon exactly the same appearances were found as in air. In particular the final intensity of the lead lines relative to those of the gold in all these cases was exactly the same, and exactly the same as that obtained with the spark in air. Further, no alteration was occasioned by using sparks as long as 3 cm., which was possible in argon, instead of 0·5 to 1 cm. as in air.

Part II.—The following lead lines were used : 3684, 3640, 2833, 2802, 2663, and 2614 A. The lines 2802 and 2833 A. are so near to gold lines that they are unusable for the determination of small concentrations of lead. Pb 2614 interferes with an iron line, although the iron line in such percentages as are likely to occur rapidly disappears on presparking. Therefore line 2614 A. should be used only when the neighbouring strong iron lines 2598·4 and 2599 A. do not appear, or are weaker than Pb 2614.

Other remarks concerning the lines used follow, together with a comparison of the spectrochemical and chemical analyses of various specimens.

Part III.—By the comparison method doubtless the most exact results can be obtained, and it has the advantage of being very convenient in practice. On the other hand, the preparation of a series of sufficiently finely graduated standard specimens is difficult.

A description follows of a method, with a table which shows how analytical results can be quickly obtained without a series of standard substances.

The substitution of an auxiliary spectrum of the simple kind described by Schweitzer (1927) was excluded by the absence of a sufficiently great number of lead lines for the comparison. The number of lead lines was therefore artificially increased to suffice for comparison with the spectrum of the basis substance. While the substitution method described earlier increases the number of lines of the basis substance, the present method increases the number of impurity lines by the reinforcement of the lead spectrum by an auxiliary spectrum. For this purpose a spectrum of tin is photographed above that of the lead-containing gold in such a way that an intensity coupling is provided between the lead and the tin. The tin spectrum is then compared with the gold spectrum, according to the method of homologous pairs. In the tin spectrum is a sharp and weak, but constant line 3656 very near the important lead line 3684 A. When the time of illumination of both spectra : lead-containing gold and tin, which are thrown directly one above the other on a single plate, is varied until these two lines have exactly the same intensity, there exists in the same spectrum pair a second tin line, 2455 A., which is of equal intensity to the other analytically important lead line. The two first lines, Sn 3656 and Pb 3684, as a result of their proximity and similar appearance, constitute a fiducial point which can be recognized with great exactness. When now the spectrum of the test-piece is correctly coupled with that of the auxiliary substance, the remainder of the spectrum of lead is replaced by the superimposed substituted spectrum of tin. Obviously, the relative intensities of the tin lines to the gold lines are then a function of the lead concentration.

The importance of a reliable method of analysis for very small contents of lead in gold is referred to by Nowack (1926).

IRON, STEEL, AND FERROUS ALLOYS.

High-purity Iron.

§ 188. High-purity Iron prepared at the National Physical Laboratory, Teddington, England.—High-purity iron is scarcely an industrial substance. Very pure iron has been produced by the National Physical Laboratory for use in researches within that laboratory and in other Government research departments for investigations of a critical character, where only iron of the nearest approach to perfect purity is adequate.

The iron in question was prepared according to the methods described by Adcock and Bristow (1935), and is the batch there referred to as Batch 4.

The analyses made were carried out by chemical methods; in cases where only faint traces of elements were found, qualitative check tests were then made by spectroscopic methods. The N.P.L. analysis which follows is, therefore, primarily a chemical analysis.

The chemical analysis revealed the following results :

Oxygen	Under 0·020 per cent.
Carbon	0·006 per cent.
Sulphur	None.
Phosphorus	Under 0·001 per cent.
Silicon	Very faint trace.
Manganese	Trace.
Nickel	0·022 per cent.
Copper	Trace.
Aluminium	Faint trace.
Iron (by difference)	Approximately 99·95 per cent.

The rods were then submitted to a critical spectrographic analysis by means of a large quartz spectrograph, using an arc between a pair of the rods, the potential across the arc being about 27 v., and the current 3·4 amp.

Approximate quantities of the impurities were ascertained by comparison with two earlier supplies of pure iron rods, when in addition to the above-mentioned elements the following were detected : chromium, cobalt, tin, vanadium, titanium, boron, and calcium (Hilger, 1932).

Further improvements in the mode of preparation of pure iron have been made recently, and they are described in a paper by Adcock (1940).

It does not appear that at the present stage industrial requirements need the application of any of the more sensitive methods of detecting impurities in steel than the simple arc described *above*.

§ 189. High-purity Iron prepared by the Westinghouse Company, U.S.A., under the Supervision of Dr. Yensen.—It may be interesting to compare the particulars of the pure iron prepared at the National Physical Laboratory with those of some prepared by the Westinghouse Company under the supervision of Dr. Yensen (Hilger, 1938). The Westinghouse Company call this " Wemco Research Iron."

In preparing this iron the refiners started from the purest electrolytic iron available, analysing 0·005 per cent. of carbon and less than this amount of sulphur and phosphorus. This iron was melted in a zircon crucible in hydrogen atmosphere. The melt was allowed to solidify in the crucible and cooled there to a low temperature. The ingot was then reheated to about 850° C. and forged into billets, which were cold-rolled to nearly the final size of the rods. These rods were annealed in dry hydrogen at 1200° C. for 20 to 30 hours, after which they were swaged to the final size.

Some of the rods come out of the furnace with a blue or slightly grey finish. This is due to the furnace being opened at 200° to 300° C., and cannot be avoided except by cooling to room temperature in the furnace with hydrogen flowing through it.

The foreign spectrum lines identified have no reference to quantity, and the majority of them are not easily found except under fairly favourable conditions using a large quartz spectrograph.

The total metallic impurities do not amount to more than about 0·01 per cent., indicating an iron content (allowing for silicon, carbon, oxygen, and sulphur) of, say, 99·97 per cent.

On the basis of experience it is supposed that the final oxygen content is less than 0·01 per cent.; the final sulphur less than 0·007 per cent.; and the final carbon less than 0·005 per cent. It should be added that the oxygen content of the rods at any time will depend upon the amount of exposure to which the iron has been subjected since leaving the laboratory.

The analysis of the metal as determined in the chemical laboratory of the Westinghouse Company was :

Sulphur . . .	0·007 per cent.
Phosphorus . . .	0·003 ,,
Manganese . . .	0·002 ,,
Silicon	0·004 ,,
Copper	0·002 ,,
Nickel	None.
Carbon and oxygen, as *above*	Less than 0·015 per cent.
Iron, by difference . .	Over 99·97 per cent.

The rods as delivered were subsequently submitted to an independent and searching chemical analysis aided by spectrographic control (the same spectrographic technique being used as in the case of the N.P.L. rods), with the under-mentioned results :

Copper	0·0008 per cent.
Molybdenum . .	0·0007 ,,
Manganese . . .	0·003 ,,
Nickel	Trace, less than 0·001 per cent.
Tin	0·0002 per cent.
Aluminium . . .	0·0001 ,,
Phosphorus . . .	0·003 ,,
Silicon	0·0023 ,,
Titanium . . .	0·0002 ,,
Silver	Very slight trace in copper precipitate.
Chromium . . .	Minute trace.
Calcium . . .	Very slight trace, about 0·00001 per cent.
Cobalt	Spectroscopic trace only in principal spectra.
Magnesium . . .	Slight trace, about 0·00005 per cent.
(Zirconium . . .	Very slight trace.)

Comparing the original analysis with this one, copper was in the former said to be 0·002 per cent., but no molybdenum was found, presumably owing to the sulphide precipitate being regarded as consisting of copper only. For the later analysis the precipitate was spectrographed, and shown to be a mixture of nearly equal quantities of copper and molybdenum.

Silicon was determined twice: 0·0022, 0·0023 per cent., by Drown's method.

Nickel, stated to be absent in the works analysis, was in good evidence in the principal spectra, although the chemical method gave 0·001 per cent. in one assay, and a negative result in the other.

Cobalt appears to be present in about the same amount.

During a general examination of the main spectrograms and of those of the precipitates, no evidence was obtained of any elements other than those mentioned as found.

Every precipitate obtained in the chemical analysis was examined spectrographically with a medium quartz spectrograph, and in this way the subsidiary traces of elements were discovered as set out *above*.

§ 189.1. Preparation of Pure Iron (Gatterer, 1937).—In this paper the author compares pure iron from several different sources.

In a later paper Gatterer and Junkes (1938) describe how they produced a very pure ferric chloride by extracting the purest analytical reagent with ether, and then precipitated it with redistilled ammonia to obtain the oxide. This was reduced in hydrogen at 600° to 700° C. to a sponge, which was then pressed and sintered to porous rectangular rods, 80 g. being so prepared. Spectrochemical analysis indicated no impurities except slight traces of copper, molybdenum, and silicon.

Another product of similar purity is under development by S. Judd Lewis. An important feature of this is that it will become available in compact metallurgical form in marketable quantities.

Steels.

§ 190. Great use has been made of the spectrograph by Barker (1939) at the Admiralty Inspection Department, Sheffield, whose technique, described *below*, doubtless depends for its success on the careful investigation of the conditions for the preparation of the spectrograms. The aim throughout Barker's work has been to test a great variety of steels for compliance with specification.

It was found that the elements present in steel in very small amounts could be estimated with a fair degree of accuracy by the internal-standard method, using the arc of 2·5 amp., but the determination of elements present in larger amounts was a very much more difficult problem.

Tables of internal standards were prepared for small amounts of several of the elements which are commonly present in steel (Table XVI).

TABLE XVI.—TABLES FOR THE SPECTROSCOPICAL DETERMINATION OF MINOR CONSTITUENTS IN STEEL.

(Wavelengths in angstroms.)

Element, per cent.	Tungsten.		Titanium.		Nickel.			
	W 4008·8.	W 2947·4.	Ti 3361·2.	Ti 3372·8.	Ni 3414·7.	Ni 3515·1.	Ni 3050·8.	Ni 3393.
0·01	...	...	...	...	Visible	...	...	...
0·02	Barely visible	...	=Fe 3359·5	...	...	...	...	...
0·05	Visible	Barely visible	...	=Fe 3372·1	=Fe 3415·5	...	...	...
0·10	...	=Fe 2947·7	=Fe 3368·8	...	...	=Fe 3516·4	=Fe 3053·1	...
0·20	...	...	...	...	...	...	...	=Fe 3392·3

Element, per cent.	Copper.		Aluminium.			Silicon.	Cobalt.	
	Cu 3247·5.	Cu 3274.	Al 3944.	Al 3961·5.	Al 3082·1.	Si 2881·6.	Co 3453·5.	Co 3502.
0·005	...	...	Barely visible	...	...	...	...	...
0·01	=Fe 3248·2	...	...	...	...	Visible	Barely visible	Barely visible
0·015	...	...	=Fe 3942·4	...	Barely visible	...	...	...
0·03	=Fe 3244·2	...	...	=Fe 3963	...	...	Visible	...
0·04	...	...	...	...	=Fe 3080	...	...	...
0·05	...	=Fe 3271	=Fe 3940·8	...	...	=Fe 2887·8	...	=Fe 3500
0·10	...	=Fe 3286·8	...	...	...	=Fe 2880·8	=Fe 3459·9	...

§ 191. Quantitative Determinations by the Microphotometer at the Admiralty Inspection Department.—The quantitative determinations of larger percentages were made by means of the microphotometer, as described in Chapter IV, but the logarithmic ratio of the galvanometer readings was plotted against percentages. The results first obtained for the determination of nickel were insufficiently accurate, so an investigation was made into the causes of the errors.

Causes of Variable Results.—From a careful review of all the conditions under which the tests were made, the factor which appeared most likely to be the cause of variation—segregation excluded—was the source of light, *i.e.* the conditions of excitation. It had frequently been noticed that during exposure the arc tended to wander, with the result that it was not focussed all the time on the centre of the slit. It was also found that during exposure an appreciable quantity of oxide was formed on the specimen, and it was thought that this might be causing interference with the arc, and thereby adversely affecting the results.

In an endeavour to overcome the effects of oxidation, experiments were made in which the arc was formed in an inert atmosphere. The results showed some improvement, but the difficulties attendant on the method were too great to warrant its being pursued.

Having investigated fairly exhaustively the suitability of arc spectra, Barker and his colleagues next turned their attention to the spark. The " standard " sparking circuit was used (§ 87). They found the optimum value of the capacity to be 0·005 μf., which was the standard condenser employed for all work on spark spectra. No inductance was used.

The first experiments with the spark, using the same kind of electrodes as those employed with the arc—namely, a rod of pure iron pointed to an angle of 80° in the upper electrode holder, and the sample of steel with a flat surface in the lower holder, the gap between the electrodes, however, being reduced from 4 to 2 mm.—although showing some improvement, were still below a standard which could be regarded as satisfactory for quantitative analysis.

The effect of substituting a rod of graphite for the pure-iron electrode was next investigated, and a very distinct improvement in results was at once apparent. Based on the results of these preliminary experiments it was possible to draw up the following conditions for spark spectra :

Wave band	2700 to 4300 A.
Slit width	0·015 mm.
Distance of electrodes from slit .	35 cm.
Spark gap	2·0 mm.
Voltage	15,000.
Added inductance . . .	Nil.
Upper electrode . . .	H.S. graphite rod, 6·5 mm. in diameter, pointed to 80°.
Lower electrode . . .	Sample steel.
Exposure	10 sec.
Plate	Zenith Supersensitive, 700 H. and D.
Development	(1) Standardized developer ; (2) time, 90 sec. at 67° F. (19·4° C.) ; (3) fixed in acid hypo for 15 min. ; (4) washed in running water for 20 min. ; (5) dried in current of warm air.

Graphs were constructed for the elements : nickel, manganese, silicon, vanadium, chromium, and molybdenum. The curve for chromium is shown in Fig. 43. Although separate curves have to be used for each element, all these elements can be estimated from the same spectrogram.

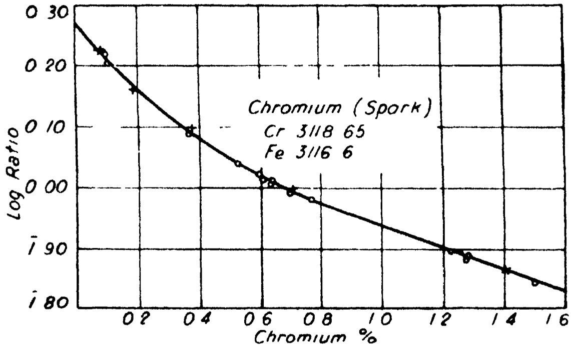

Fig. 43.—Standard Curve for the Estimation of Chromium from Spark Spectrograms.

§ 192. Effect of Variables in the Technique.—Having arrived at what appeared to be a satisfactory technique, the author next determined the extent to which the accuracy would be affected by varying the standard conditions.

Variation in Exposure.—For this purpose spectrograms were prepared under the standard conditions of exposure—*i.e.* 10 sec.—from 10 different samples of steel, the nickel content of which covered the range 2·03 to 4·37 per cent. A standard curve for nickel was plotted from these. Then a similar series of spectrograms was prepared from exposures of 3, 6, and 15 sec. respectively. These were then read, and the results showed that an exposure of 3 sec. tends to give high values with the lower percentages of nickel and low values with higher percentages. With 15-sec. exposures there is little difference on low percentages, but with high percentages the values increase. The results obtained for 6-sec. exposures are generally in very good agreement with those obtained under standard conditions. Since in practice there is found to be no difficulty in controlling the time of exposure within one second, it is clear that there is little risk of variable results due to such variations in exposure as are likely to occur.

Variation in Time and Temperature of Development.—In these tests one series of spectrograms was developed for 75 sec. and another for 105 sec., both at the standard temperature. Another series was developed at a temperature of 62° F. (16·7° C.) and another at 72° F. (22·2° C.), both for the standard time. A further series of tests was made to determine the effect of using a very stale developing solution. The results demonstrate that when the nickel content is low, short exposures tend to give high results and long exposures low results. Similarly, when the nickel content is high, short exposures tend to give low results and long exposures high results.

The effect of variation in temperature follows similar lines. When the nickel content is low, a low temperature tends to give high results and a high temperature low results, and when the nickel content is high the reverse occurs. The effect of the stale developing solution is, as would be expected, similar to that obtained from a short exposure, a short period of development, or development at a low temperature. The solution used for this test was artificially aged by standing in an unstoppered bottle and being frequently shaken to accelerate oxidation. Its condition would be equivalent to that of developer many months old, and it was obvious from its colour that it was quite unsuitable for use. The volume of the solution usually made lasts about three weeks, and tests on standard steels have shown that the results are not affected by any changes which occur during that period.

Excluding the results obtained with the stale developer, none of the figures for the nickel content differs very seriously from those obtained by chemical analysis. Further, since no difficulty is experienced in timing the development within ± 2 sec. nor in maintaining the temperature of the developer within ± 2° F., it is clear that the liability to error on account of variation in the time or temperature of development can be ignored. If in summer difficulty should be experienced in maintaining temperatures as low as 67° F., a new series of curves could be constructed for any temperature that it was considered desirable to adopt.

§ 193. *Effect of Preliminary Sparking.*—This was studied because certain workers who have investigated the suitability of spectrochemical methods for the analysis of aluminium and its alloys have reported improved results when they employed a preliminary sparking period. Tests were first made in the normal manner, by giving a 10-sec. exposure immediately the spark was struck. Then further tests were made, in which the spark was allowed to run for 30, 60, 90, 120, and 150 sec. before the 10-sec. exposure was made. Four exposures were made for each condition of test, and the maximum and minimum deviations from the averages of these were obtained. The results indicate that, as regards steel analysis, the preliminary sparking period has very little influence on the results.

§ 194. *Influence of Shape and Material of Upper Electrode.*—The shape and composition of the electrodes used for these tests and the accuracy obtained on samples with nickel contents up to 4 per cent. are shown in Table XVII. It will be seen that no electrode gives more consistent results than the pointed graphite

TABLE XVII.—INFLUENCE OF MATERIAL AND SHAPE OF UPPER ELECTRODE.

(Results with respect to nickel contents in steels.)

Material.	Shape of End.	Accuracy* (for Ni up to 4 °/₀), per cent.	General Observations.
Sample steel	Pointed	± 0·20	Exposures uneven.
Graphite	Pointed	± 0·09	Even exposures.
	Chisel-edged	± 0·09	Tendency to preferential sparking.
	Flat	± 0·15	Tendency to preferential sparking, also uneven exposures, and lines diffuse.
	Spherical	± 0·20	Tendency to preferential sparking.
Silver	Pointed	± 0·09	Slightly more background than with graphite electrode.
Pure iron	Pointed	± 0·20	Exposures uneven.
	Chisel-edged	± 0·50	Exposures uneven and preferential sparking.
	Flat	Poor	Exposures uneven and preferential sparking.

* Variations are expressed as percentages of the total steel.

one which was adopted as standard for spark-spectra work on steel. The worst results were obtained with a pure-iron electrode cut to a chisel edge, and this is attributed to the great and uneven strengthening of the iron line relative to the nickel line, and to the irregular and preferential sparking which occurs along the chisel edge. The flat-ended iron electrode also gave very poor results, and these were obviously caused by preferential sparking.

Silver gave a result very similar to graphite, and as a rod of silver costs more than one of graphite it appeared at first that no advantage would be gained from its use. Experience since the paper was published, however, has shown that silver rods possess advantages, in that they keep their point much longer than those of graphite, they require less frequent sharpening, the wastage is less, and on routine work they have been found more economical.

§ 195. *Effect of Physical Condition.*—Three conditions were tested, namely, fully annealed, hardened, and hardened and tempered. The results set forth in the paper indicate that, in the case of steels, the physical condition of the metal does not influence the results of spectrochemical analysis for silicon, manganese, nickel, chromium, molybdenum, and vanadium. The difference between the averages of each of the series of tests is within the limits of normal experimental error for this method of estimation.

§ 196. *Heterogeneity.*—The degree of heterogeneity exhibited by forged or rolled steel is dependent upon several factors, such as the condition of the metal at the time of tapping, the rate of pouring, the rate of solidification, and the amount and nature of the work subsequently done upon it. Although in bars and small forgings the original as-cast structure is well broken down, in large forgings, where a relatively small amount of work is done, the breakdown is not so complete, and heterogeneity is more evident. As a large amount of the work consisted in determining the chemical composition of large forgings, the samples required for the investigation were taken from them.

Examination of a forging which has been sparked shows that only a very small amount of metal is volatilized during the sparking, and from the fact that the pattern developed by etching is caused by differences in chemical composition, it will be obvious that variations in spectrochemical results are likely to be obtained if only one spot is examined, even though the most perfect technique is employed. On this account a standard practice was adopted for routine work of making three exposures on each sample and taking the average figure of the three results. If the three results obtained differ by more than a given amount a further set of three exposures is made. In case this appears a tedious process, it may be restated that an exposure takes only 10 sec., and the photo-electric reading of a line pair only 30 sec.

§ 197. Accuracy of the Method.—The accuracy of this method may be judged by Table XVIII, in which are compared the chemical and spectrochemical results obtained on fifty consecutive samples of nickel-chromium-molybdenum steel which were received for analysis. The two series of tests were carried out by different men and quite independently of each other.

TABLE XVIII.—COMPARISON OF RESULTS OF CHEMICAL AND SPECTROCHEMICAL TESTS ON SAMPLES OF NICKEL-CHROMIUM-MOLYBDENUM STEEL.

(Tests on 50 consecutive steel samples received for analysis, all of which were analysed chemically and by the spectrograph.)

Element.	Range covered, per cent.*	Accuracy.*
Silicon .	0·05 to 0·30	All spectro results fell within ± 0·015 per cent. of chemical figure.
Manganese .	0·20 to 0·70	48 spectro results fell within ± 0·02 per cent. of chemical figure. 2 spectro results were 0·10 per cent. lower than chemical figure.
Nickel .	2·5 to 3·5	48 spectro results fell within ± 0·10 per cent. of chemical figure. 1 spectro result was 0·25 per cent. lower, 1 spectro result was 0·25 per cent. higher, than chemical figure.
Chromium .	0·50 to 1·2	48 spectro results fell within ± 0·02 per cent. of chemical figure. 1 spectro result was 0·05 per cent. higher, 1 spectro result was 0·05 per cent. lower, than chemical figure.
Molybdenum	0·20 to 0·60	48 spectro results fell within ± 0·03 per cent. of chemical figure. 1 spectro result was 0·10 per cent. higher, 1 spectro result was 0·12 per cent. lower, than chemical figure.

The effects of segregates were examined by positioning the centres of segregates immediately below the point of the top electrode and then sparking in the usual manner. Tests were also made in positions which appeared to be clear of the segregates. The results give a very clear indication as to the metals which segregate most in steels of this class. These are shown to be manganese and molybdenum. It is known that the segregates also contain carbon and sulphur in excess of the amount present in the normal metal, but this information was not obtained spectrographically.

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* Percentages of the total steel.

§ 198. The range of alloy steels analysed at the Admiralty Inspection Laboratory by routine spectrochemical methods and the accuracy claimed, except in special cases where the sample under test contains very large segregates, are indicated in Table XIX.

TABLE XIX.—STEELS ANALYSED BY SPECTROCHEMICAL METHODS AND THE ACCURACY ATTAINABLE.

(Contents as percentages.)

Type of Steel.	Si.	Mn.	Ni.	Cr.	Mo.	V.	Ti.	Co.	Cu.	Al.
Carbon . .	0·01–0·30	0·01–0·80	0·01–1·00	0·01–0·10	0·01–0·10	0·01–0·10	0·01–0·10	0·01–0·10	0·005–0·10	0·005–0·05
Nickel . .	,,	,,	1·00–4·5	,,	,,	,,	,,	,,	,,	,,
Ni–Cr . .	,,	,,	,,	0·10–1·50	,,	,,	,,	,,	,,	,,
Ni–Cr–Mo–V .	,,	,,	,,	,,	0·10–0·70	0·10–0·25	,,	,,	,,	,,
Mn–Mo . .	,,	1·3–1·9	0·01–1·00	0·01–0·10	0·10–0·40	0·01–0 10	,,	,,	,,	,,
Accuracy attainable at Percentage Contents shown, per cent. of total steel.										
Content . .	0·30	0·80	3·50	0·80	0·70	0·25	0·10	0·10	0·10	0·05
Accuracy .	±0·02	±0·05	±0·10	±0·04	±0·05	±0·02	±0·02	±0·02	±0·02	±0·01

The reason for the success in the technique described *above* seems to lie in the attention given to detail and standardization of routine. This is not of an extreme or meticulous character, and involves only reasonable attention to a number of details. There is nothing in the method which requires an undue amount of pains or time, but Barker has taken the different items of technique, tried different ways of carrying them out, and then selected the most convenient and rapid one which would give good results, and adhered to it.

Two facts which appear to be new and of practical importance were established in this research. The first (not mentioned in the paper) was that inclusions produce a preferential action in the spark *when inductance is used.* The second was concerned with the question of speed. Most workers had been in the habit of giving a considerable amount of time to presparking before commencing the photographic exposure of each specimen, and some authorities said that for light alloys it was desirable to spark for five or even seven minutes before taking the photograph. It was found that presparking is unnecessary in the case of steels.

Since Barker's paper was published his laboratory has conducted further experiments on the spectrochemical analysis of steel. The spark technique has been modified, and instead of taking the average result of three separate spectrograms of a sample, the result is obtained from a single spectrogram of six superimposed exposures at different positions on the sample surface. One graphite electrode suffices for three exposures, or two graphite rods per spectrogram. A slower-speed plate has been adopted, which has proved an advantage. The increased time taken in making the exposures is compensated for by the decreased number of spectrograms to be evaluated photometrically, and the method has generally improved the accuracy and reliability of the results.

The revised technique is given *below* :

Wave band	2700 to 4300 A.
Slit width	0·015 mm.
Distance of electrodes from slit	38 cm.
Quartz condenser	2 cm. from slit, forming an image of the spark on the face of the collimator lens.
Spark gap	2·0 mm.
Applied voltage	15,000.
Added capacity	0·005 μf.
Added inductance	Nil.
Upper electrode	H.S. graphite rod or silver rod, ¼ in. in diameter, pointed to 80°.
Lower electrode	Sample of steel with filed surface horizontal.
Exposure	90 sec. : six superimposed exposures of 15 sec. each taken from different positions on the filed horizontal surface of the sample.
Plate	Ilford Thin-film Half-tone.
Development	(1) Standard developer ; (2) time 90 sec. at 67° F. (19·4° C.) ; (3) fixed in hardened acid hypo for 7 min. ; (4) washed in running water for 10 min. ; (5) dried in a current of warm air.

§ 198.1. Carbon in Steel (Gatterer and Junkes, 1938).—These authors point out that carbon is one of the constituents whose quantitative determination is attended with great difficulties, since it possesses few lines, and of these a number, diffuse in themselves, nearly coincide with iron lines or lie in the Schumann region of the spectrum, which is not accessible to any but a vacuum spectrograph.

They give a résumé of previous work on the spectrochemical determination of carbon in iron, and give particulars of the spectrochemical determinations of steels containing 0·16 to 1·47 per cent. of carbon, comparing them with the chemical determinations.

§ 198. 2. Aluminium in Steel.—Hartleif (1940) points out that the gravimetric determination of very small amounts of aluminium in steel is very lengthy. Not only is the separation of the aluminium slow, but there are often other alloying elements which can be separated from aluminium only by tedious methods. He therefore used spectrochemical analysis for his problem, which was that of determining the total aluminium content of the melt, the aluminium being present in very small percentages.

Attention had to be given to the fact that the aluminium, added as a deoxidizer, partly burns to alumina, which is present in the steel either combined with iron oxide or pure. The alumina, particularly the uncombined portion, segregates when the steel is cast in the usual ingots, and it is then frequently found in the form of veins.

In order that the spectrochemical determination may represent the correct total percentage of aluminium, means must be employed of making homogeneous specimens. It was found that the samples as normally ladled for the chemical analysis are satisfactory if cast in very small chill moulds and then forged to bars about 15 mm. × 30 mm. section. Owing to the small volume of the mould the steel becomes solid almost instantaneously, and segregation does not take place (see § 235). Even when the steel after rolling shows strong veins these are not notably rich in aluminium.

For contents of from 0·005 to 0·06 per cent. of aluminium, the line 3961·5 proved quite suitable with the iron line 3963·1 A., although the molybdenum line 3961·40 interferes with the former if more than 0·2 per cent. of molybdenum is present, and the chromium line 3963·69 interferes with the iron line if more than 0·2 per cent. of chromium is present. Both lines are affected by variations of the sparking conditions in the same manner.

Only one of the electrodes is of the specimen to be analysed, and this must have end surfaces of a standard degree of roughness, since it was found that the presparking time, *i.e.* the sparking time until constant conditions are reached, depends on the surface qualities. The roughness of the surface is determined by the grain of the file used. The flat end surface should be larger than the area covered by the spark, though exact sizes need not be adhered to, since the area over which the spark ranges is determined by the diameter of the second electrode and the spark gap. The second electrode was of electrolytic copper 4 mm. in diameter, the spark gap being about 3·5 mm. The spark was produced by a Feussner set with 0·0033 μf. capacity and 0·8 mh. self-induction. In order to reduce the exposure time, instead of the middle of the spark the third of the spark adjoining the iron electrode was imaged, enlarged about three times, on to a 5-mm. high intermediate diaphragm.

Tables are given indicating the error for samples with various aluminium contents.

The paper ends with a consideration of what the effect may be of the different vapour pressures of the dissolved aluminium and of the alumina.

It may be pointed out that the effect of aluminium on the properties of steel depends on the form in which it is present, *i.e.* whether it is in solution or present as particles of alumina. The method described *above* does not, of course, discriminate between these two forms.

Super-rapid Analysis of Cast Iron.

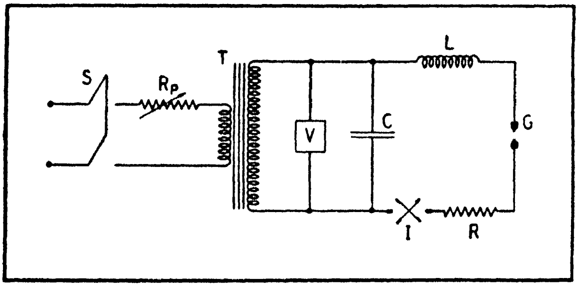
§ 199. Vincent and Sawyer (1937, 1938, and 1939) and Vincent, Sawyer and Sampson (1938) had quite a different problem to solve. They developed their process for the plant of the Campbell, Wyant and Cannon Foundry Company, of Muskegon, Michigan, U.S.A., and arrived at a technique whereby six elements (chromium, copper, manganese, molybdenum, nickel, and silicon) were determined quickly enough for controlling the slow changes, or "drifts," in the concentration of the several alloying constituents in the molten iron in the furnace or cupola. If these are to be maintained within narrow limits of tolerance, it is of vital importance that the time elapsed between the pouring of a sample of the iron and the posting of the analysis results should be as brief as possible; otherwise, a control of drifts is not provided, and only an inspection analysis results. The procedure permits the analysis of a sample of cast iron for the above six elements in seven minutes elapsed time, while the accuracy exceeds that of the routine chemical wet methods previously used.

A distinctive feature of the technique is the method of rapid processing worked out by the authors in collaboration with the Eastman Kodak Company, requiring only about three minutes for processing and drying (Vincent and Sawyer, 1939).

The percentage ranges of the constituents covered, which comprise all current cast irons in the foundry company's production, are as follows :

	Per cent.
Chromium	0·01 to 1·50.
Copper	0·20 to 3·00.
Manganese	0·30 to 1·25.
Molybdenum	0·07 to 1·50.
Nickel	0·15 to 2·00.
Silicon	0·50 to 4·00.

The authors used a condensed spark. In the circuit (Fig. 44) are a loading inductance L, a synchronous rotary interrupter I to allow sparking at the peak voltage only, and a damping resistance R ; a quenching air blast is employed to chop off the oscillations before the discharge becomes arc-like in character. The result is a discharge which is so uniform in its evaporation and excitation of the various electrode constituents that the authors believe the accuracy to be limited only by the plate variations and by the microphotometer errors.



C	Condenser.	R_p	Adjustable primary resistance.
G	Sample gap.	S	Mains switch.
I	Synchronous interrupter.	T	High-voltage transformer.
L	Inductance.	V	Electrostatic voltmeter.
R	Resistance.		

Fig. 44.—Circuit Diagram of Condensed Spark Source.

They rejected the use of the D.C. arc owing to the production thereby of subsurface boiling (Fig. 45).

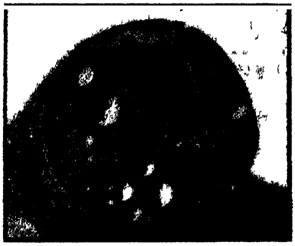


Fig. 45.—End of Electrode burned in D.C. Arc showing evidence of Subsurface Boiling.

It may be mentioned that an interesting type of large quartz spectrograph to the specification of Vincent and Sawyer is under construction for the Ford Motor Works, Rouge Plate, Detroit, Michigan, U.S.A., to meet the requirements of super-rapid analysis. This instrument takes the whole spectrum range from 2125 to 3300 A. on a single film 16 in. long, this containing all the lines required for analysis in the plant in question. With this dispersion the line Cr 2677·17 is well resolved from Fe 2678·88.

Other Investigations on the Spectrochemical Analysis of Iron and Steels.

§ 200. *Twyman and Fitch* (1930) used spark spectra and a logarithmic sector, similar to that described by Scheibe and Neuhäusser (1928), in their work on the determination of copper, silicon, manganese, nickel, chromium, molybdenum, and vanadium in steels. A series of 20 steels containing various percentages of the elements in question was prepared by Kayser, Ellison and Company, and very careful analyses were made at Sheffield University under the direction of Professor C. H. Desch. The authors gave graphs in which the differences in the lengths of the spectrum lines (produced by the use of the logarithmic sector) are plotted against percentages of the constituent, and they were of the opinion that the following accuracies could be obtained by them :

	Per cent.
Silicon	10
Chromium	5
Nickel	5
Copper	5

Twyman and Harvey (1932) investigated the spectrochemical estimation of manganese, nickel, and chromium in steels, using the arc, their endeavour being to find a form of plotting the results which would yield graphs available over a larger range of percentages, without the necessity of using such a large number of standard specimens. It was found that, over considerable ranges, when the line length was plotted against the logarithmic percentage, a straight-line graph was obtained; this form of plotting has been very generally adopted since that time (it was used earlier by Lomakin, 1930). (The method of deriving line intensities from the lengths of line obtained with the logarithmic sector is given by Twyman and Harvey, 1931.) The same series of steels was employed as in the investigation by Twyman and Fitch.

Rivas (1937) carried through an extensive research with a low-alloy steel. His method makes use of solutions to avoid the difficulty of heterogeneity, and may be summed up as follows:

The "weighed-out" quantity is dissolved in nitric acid, the nitric fumes are boiled away, and the solution is made up to a definite volume. The concentrations employed are from 0·08 to 0·1 g. of steel in 1 ml. of solution. The determination proceeds as follows: Pieces 8 to 9 mm. long are cut from spectroscopically pure carbons, and these are flattened on the ends and held in tweezers fixed in the electrode holder. The carbons are heated by presparking, and then by means of a micropipette 0·01 ml. of the solution is placed on each carbon. Such quantities of liquid are quickly soaked up by the carbons. Then the exposure is made, and the plate developed as usual. The selected lines of the basis metal and the element to be determined are photometered, and evaluated by means of a spectrogram taken with the standard solution. The method of employing the microphotometer was somewhat unusual.

Rivas obtained very satisfactory results with this technique. In determining nickel in iron (with a content of 0·32 per cent. of nickel) he gets an average proportional error of 1·9 per cent. and a maximum error of 4·2 per cent.

The following investigations are also of interest:

§ 201. *Scheibe and Schöntag* (1934).—See § 135.

Heidhausen (1937), using a Feussner spark (§ 87. 1, *b*) and a microphotometer, describes the apparatus and routine for the daily control of materials in machine construction. The results of the determination of silicon in grey cast iron show that the errors in the ordinary chemical determination (not using the methods of exact analysis) and the spectrochemical methods are about the same. The author concludes by saying that, since obtaining the results set forth in the paper, his laboratory has obtained an increase in uniformity of the results by paying more attention to the electrodes of the rotating interrupter.

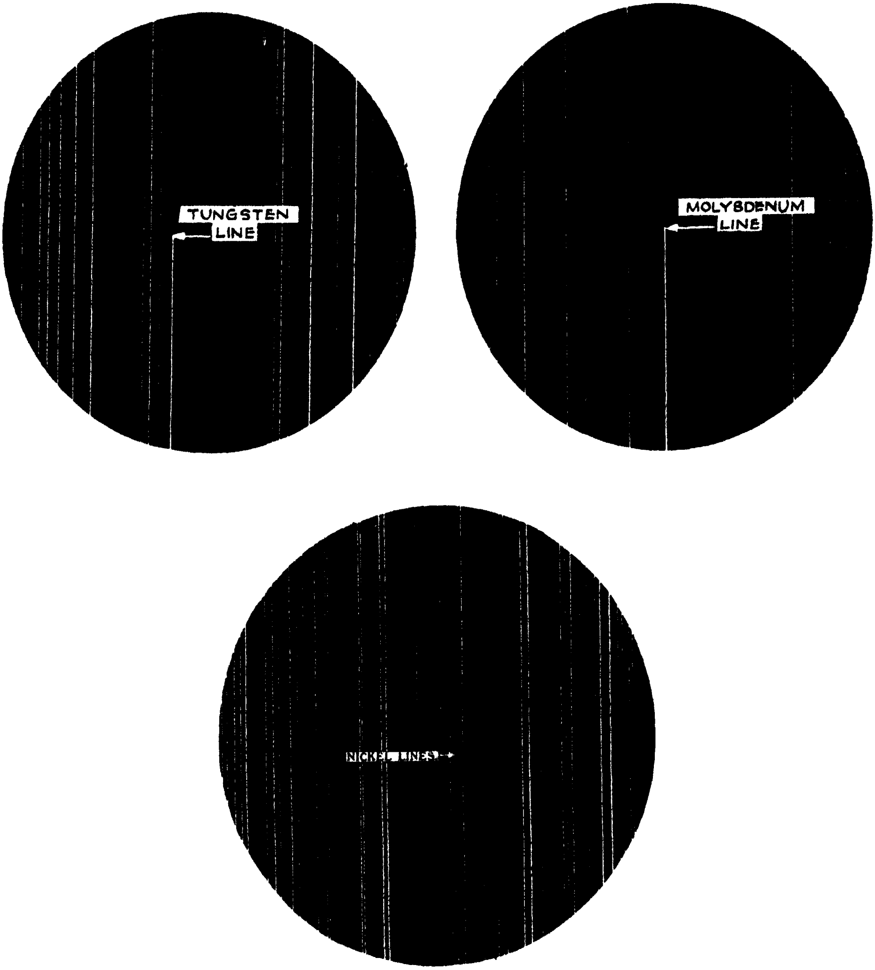
Rapid Analysis of Alloy Steels by Visual Inspection.

§ 202. It is of interest to note that the first attempt at the quantitative analysis of steels by spectrochemical analysis was made by Sir J. G. N. Alleyne in 1875, when he communicated a paper on the estimation of small quantities of phosphorus in iron and steel by spectrochemical analysis to the Iron and Steel Institute. His procedure was somewhat involved, and consisted in locating the phosphorus lines by observing a carbon spark with phosphorus in the crater. The spark spectrum of the steel sample was observed in an atmosphere of hydrogen in a glass vessel, when the phosphorus lines were not seen. This vessel was connected to an aspirator and a carbon-dioxide generator. The hydrogen was replaced gradually by carbon dioxide, and the amount of carbon dioxide introduced before the phosphorus lines appeared was measured. These figures were plotted against the percentage of phosphorus, giving standard curves to which observations on unknown steels were referred.

In 1923 the present writer designed an instrument for Messrs. Vickers Ltd. (now the English Steel Corporation) to solve the problem of selecting scrap in the scrap-yard for remelting. A grating instrument, it gave enough dispersion for percentages of nickel and chromium to be roughly estimated by comparing their lines with neighbouring lines of iron. This appears to be the first practical application in industry of the internal-standard method described by Gerlach several years later (§ 117).

A later, two-prism form, now well known as the " Steeloscope," was arranged to deal in the same way with nickel, chromium, molybdenum, manganese, titanium, tungsten, cobalt, copper, tin, cadmium, and vanadium. It has been found that with experience non-technical workers can discriminate at once between different varieties of steel with sufficient accuracy to serve a very valuable purpose in checking steel stores, purchases, and scrap. A movable eyepiece can be set opposite to a mark corresponding to the metal to be determined, when a distinctive line of that metal comes into the middle of the eyepiece, and its intensity can be compared with that of a neighbouring iron line. A number of charts similar to those reproduced in Figs. 46 to 48 enable the observer to recognize the lines.

The kinds of discrimination that can be made are given *below*; they were actually made by a member of a research staff. It should be noted that unskilled lads readily attain, after a week or so, an accuracy far greater than can be obtained even by a qualified skilled observer who has had but a few hours' experience with a particular range of steels.



Figs. 46 to 48.—Visual Spectra obtained with Alloy Steel.

Cobalt.—Discrimination was successfully made between steels containing 19·8, 6·0, 3·0, and 2·47 per cent. of cobalt.

Molybdenum.—Discrimination was successfully made between steels containing 7·3, 2·25, 1·0, and 0·57 per cent. of molybdenum. Two settings of the eyepiece are provided for the detection of molybdenum, Mo I being for low percentage contents (less than 1), and Mo II for percentage contents above 1.

Tungsten.—Discrimination was successfully made between steels containing 16, 5·86, 4·0, and 0·42 per cent. of tungsten. The difference between the 5·86 and 4·0 per cent. samples was small. The arc current for the detection of tungsten must be not less than 5 amp.

Vanadium.—Discrimination was successfully made between steels containing 1·4, 0·87, 0·24, and 0·19 per cent. of vanadium. Little difference in intensity was shown between the two higher-content samples, but there was very distinct difference between the two higher and the two lower samples. The group of lines selected in the instrument will detect less than 0·1 per cent.

Manganese.—The line chosen for the detection of manganese will enable rough quantitative measurements to be made up to 0·7 per cent. Above this content another setting of the eyepiece is available, which enables quantitative measurements to be obtained between 0·6 and 1·4 per cent.

Titanium.—Discrimination was easily possible between three samples examined, containing 1·9, 0·636, and 0·168 per cent. From these observations it is thought that titanium samples with a contents ratio of 2 could be differentiated. 0·054 per cent. of titanium was easily detected in some small turnings.

Cadmium and Tin.—Samples containing these metals were not available at the time of test, but the Steeloscope provides for their detection, though what percentages can be detected, and with what accuracy, has not yet been ascertained.

Chromium.—In addition to the usual setting, the eyepiece can be set for a chromium line which will allow quantitative estimation of this metal between 0·5 and 3·0 per cent. Discrimination has been successfully made between the following samples: 3·01, 2·22, 1·55, 1·23, 0·79, and 0·41 per cent.

It will be noted that the principle of the internal standard is implied in the use of this instrument, which in its simpler form was first made in 1923. The instrument is now in extensive use, but I am not acquainted with any description in a technical journal, except that by Kjerrman, Phragmén and Rinman (1937).

§ 203. An eyepiece called the "Insta" eyepiece is made for increasing the accuracy of such determinations as the above. This also was designed by the present writer, but his personal opinion is that by using it the advantage of great speed is to some extent lost, and the instrument is no longer suitable for being used by workers untrained in the handling of scientific instruments.

Scheibe and Limmer (1932) described a visual spectrometer with a photometric attachment based on the polarizing principle, by which visual determinations could be made of the percentages of chromium, molybdenum, titanium, copper, magnesium, barium, nickel, manganese, vanadium, zinc, and silicon. The instrument in effect (though not in photometric principle) was very similar to the Steeloscope with Insta eyepiece.

§ 204. The Spectrograph in the Iron Foundry.— Illustrations of the layout of the spectrographic laboratory, the light-source room, the dark-room, the microphotometer equipment, and the method of pouring samples from the ladle, in the foundry, are given by Vincent, Sawyer and Sampson (1938) –see Fig. 41, § 161. 6.

LEAD AND ITS ALLOYS.

§ 205. The chemical analysis of lead for its impurities is a long and expensive business. For example, it would take an analytical chemist approximately one week to obtain a complete analysis of a sample of lead. To arrive at the results more rapidly would necessitate the employment of a staff of several additional expert analysts, and even then the time would be greatly in excess of that required for the spectrographic determination of the same number of impurities.

In manufacturing, apart from the employment of the spectrograph for rapidly ascertaining the composition of lead or lead alloys, the apparatus can be used extensively in other directions. For example, a rapid analysis can be made of a representative sample of metal in order to decide whether it is suitable for use, and a price thus quoted for the batch, if acceptable, on the same day.

When various consignments of scrap lead are melted down in large batches, a sample ingot can be taken from each cast and submitted for analysis. Upon the results obtained, the amount of remelted scrap lead, containing, say, a certain percentage of tin, to be added to a charge of pure lead in order to produce a specified alloy can be ascertained. Working on the same figures, the quantities of undesirable impurities can be reduced below the permissible amounts in a specification. The control of impurities is essential when producing material conforming to the British Standard Specification for lead pipe and also for the B.N.F. ternary alloys of lead.

High-grade Lead.

§ 206. At the works of Messrs. Mellowes and Company, Sheffield, the small quartz spectrograph is used to determine the following impurities and alloying elements over the ranges indicated :

	Per cent
Copper	0·0002 to 0·1
Silver	0·0008 to 0·005
Bismuth	0·0005 to 0·5
Antimony	0·01 to 1·0
Zinc	0·001 to 0·4
Cadmium	0·0008 to 0·4
Tin	0·001 to approx. 3·0

Pirelli-General Cable Works, Limited, Southampton, use the spectrograph for the routine examination of pig-lead of purity 99·99+ per cent. for use in cable-sheathing and for the manufacture in their own works of most of the accepted cable-sheathing alloys. The arc or spark spectrum is employed with internal (§ 117) or " auxiliary " (§ 119) standards, and the impurities, mainly antimony, copper, silver, bismuth, and zinc, are determined down to 0·001 per cent., or in some cases 0·0005 per cent.

§ 206. 1. The Spectrographic Analysis of Lead as carried out in the Laboratory of the British Non-ferrous Metals Research Association.—For the routine analysis of lead, the spark spectrum of the sample under test is compared with that of an auxiliary alloy of lead with a known small quantity of tin. The tin lines in the auxiliary spectrum serve as intensity standards, and by this means analytical tables have been compiled for the determination of the principal impurities to the lower limits quoted in Table XX. This method was first described by D. M. Smith (1933), and is still in use as a rapid routine method of analysis.

It is their experience that the results of different observers, using the same analytical tables of the <, =, > type (*cf.* Table VI, § 119), agree more closely than when the internal-standard method alone is used.

TABLE XX.—LIMITS OF DETECTION OF IMPURITIES IN LEAD (B.N.F.M.R.A.).

Element.	Limit of Detection, per cent.	Element.	Limit of Detection per cent.
Antimony	0·005	Silver	0·0001
Arsenic	0·01 (estimated)	Tellurium	0·005 (estimated)
Bismuth	0·0002	Tin	0·003
Cadmium	Less than 0·0001	Zinc	0·001 (estimated)
Copper	0·0001		

With the provision of standards of accurately known composition, other elements, *e.g.* nickel, cobalt, mercury, etc., could also be determined by the same method.

In the case of the determination of antimony, which is of importance, the use of arc spectra was studied in the hope of materially increasing the sensitivity of detection, but the limit was only extended to 0·003 per cent. by this means.

Analysis of Electrolytic Lead.—In a paper entitled "On Methods of Testing the Purity of High-grade Lead," by R. S. Russell (1932), it is stated that the spectrographic method is not sensitive enough to check the purity of electrolytic lead. I have not been able to consult the paper to see whether use was made of the most sensitive methods available.

Alloys of Lead.

§ 207. Brownsdon and van Someren (1931) give a simple routine for the spectrographic examination of lead and lead alloys, using the internal-standard method. The paper gives tables for rapid approximate estimations of the following impurities in lead and lead alloys:

	Per cent.
Tin	0·002 to 9·0
Antimony	0·03 to 15
Arsenic	0·03 to 1·5
Bismuth	0·0003 to 0·15
Copper	0·0002 to 0·06
Zinc	0·001 to 0·06
Silver	0·0006 to 0·002
Cadmium	0·0003 to 1·0

D. M. Smith (1931) gives particulars of the preparation of standard samples and tables for rapid quantitative analysis of alloys with the logarithmic sector, with particular application to the analysis of ternary alloys of lead. He concludes that, for the routine analysis of ternary alloys of lead within the range of composition usual for cable-sheathing, lead-pipe, and sheet production, spark spectra are more suitable than arc spectra, and considers that with the routine described an accuracy of ± 10 per cent. is attained by the simple method of direct comparison of spectra, with some improvement of accuracy if the logarithmic sector is used.

As a result of this work, supplemented by an investigation carried out by the Post Office Research Laboratory, use is made of the spectrograph throughout the electric-cable making industry of Great Britain in the analysis of lead and its binary and ternary alloys. D. M. Smith tells me he would now advise the use of the microphotometer, and sends me the following account of the method he now uses in the laboratory of the British Non-ferrous Metals Research Association :

§ 207. 1. The Accurate Spectrographic Determination of Antimony in Lead-Antimony Alloys by means of the Microphotometer.—The principal results of an investigation on the spectrographic determination of antimony in binary lead-antimony alloys, over the range 0·2 to 1·2 per cent. of antimony, may be briefly summarized as follows :

(1) *Recommended Technique.*—Measurement of the relative (photometric) densities of the line pair Sb 2598·1 : Pb 2628·3 in spectra of the spark between stationary electrodes (following standard practice) is recommended.

The accuracy claimed by Badum and Leilich (1937), who used the line pair Sb 2311·5 : Pb 2332·5, has not been confirmed.

(2) *Use of Rotating Electrodes.*—Rotating disc electrodes of 2-mm. thickness and 3·5-cm. diameter, arranged so that the spark discharge passed between two edges rotating in opposite directions, were tested from the point of view of analytical accuracy.

Considerably larger errors were, however, obtained when using this procedure. An explanation may perhaps be sought from the observation of Badum and Leilich (*loc. cit.*) that the distance between the electrodes has a measurable influence on the density ratios. It is probably more difficult to ensure a constant spark gap between rotating discs than between stationary electrodes.

(3) *Effect of Metallurgical Condition of the Samples.*—Systematic

deviations between the analyses of extruded and cast samples of antimonial lead (cable-sheathing alloys) have been traced to the effect of the metallurgical condition on the density ratios in spark spectra, giving a somewhat different slope to the log $R \propto$ log *per cent.* calibration curve. For accurate analyses, therefore, both standard alloys and samples under test should be in a similar metallurgical condition, *e.g.* either extruded or cast, in each case.

(4) " *Variant-exposure* " *Method.*—In an attempt to improve the accuracy attainable from measurements on individual spectra, the application of the "variant-exposure" method of Whalley (1937), first used in the analysis of magnesium alloys, was tried. The derivation of a correction to be applied to the photographic-density ratios, to compensate for variations in the blackening of the spectra, did not lead to any increase in analytical accuracy. The validity of the "variant-exposure" method, however, was confirmed, as also McClelland and Whalley's statement (1939) that this method is only usefully applied in cases where lines of widely different intensities are being compared.

(5) *Analytical Accuracy.*—Following the recommended technique, reproducibility tests on an alloy containing 0·51 per cent. of antimony showed a "standard error" (determined by the formal statistical method) of 2·2 per cent. of the actual content, in individual determinations. A detailed comparison of spectrographic and chemical analyses of seven antimonial lead alloys, covering the range 0·6 to 1·2 per cent. of antimony, gave an average deviation of 3·3 per cent. of the content as determined chemically. The use of three determinations on each sample reduced the "average error," based on two series of tests, to 1·3 and 1·9 per cent. respectively.

It is therefore concluded that with the proposed procedure of analysis (microphotometric interpolation between known standards), in which the mean of three determinations on each sample would be used, the average analytical error obtained in routine practice should not exceed 2 per cent. of the actual antimony content.

§ 207. 2. A tentative method of test for copper, bismuth, silver, nickel, antimony, tin, and cadmium in high-grade pig lead has been published by the American Society for Testing Materials (1937). The method is based on that of Nitchie and Standen (1932). Weighed turnings or filings are dissolved in nitric acid, and the solution is introduced into a hole in the graphite electrode of an arc. Comparison is made with spectrograms of standard solutions.

§ 208. Breckpot (1937*b*) points out that not only is the chemical analysis of lead very long and difficult, but that also industrial laboratories regularly recorded in the chemical analysis of pure lead 15 to 20 g. of zinc per ton when the actual amount present was only about one-twentieth of that amount. He describes a technique which, he says, is in use in several important metallurgical works as a routine method for the determination of bismuth, silver, copper, cadmium, thallium, indium, arsenic, antimony, and tin in binary alloys of lead. He also studied (Breckpot, Creffier and Perlingh, 1937) the ternary system lead-tin-antimony, with amounts of tin and antimony varying from 0·1 to 3 per cent., to ascertain the effect of variation of the percentage of one on the determination of the other. This paper deals also with the determination in such alloys of bismuth, indium, silver, copper, cadmium, and arsenic. In another paper (1937*a*) he deals with the determination of thallium and bismuth.

Although Breckpot prefers, with the analysis of most metals, to convert them into oxides by the method described elsewhere (Breckpot and Mevis, 1935*a*), he recommends that lead should be analysed by a direct arc between the metallic electrodes. One of the reasons for this is that a transformation of the lead from the nitrate into the form of oxide of homogeneous composition presents certain difficulties, and further that an arc formed on lead oxide is not very stable. He finds that an arc of 1 amp. can be maintained very well between lead electrodes if one takes the following precautions: (*a*) to have the electrodes sufficiently massive to avoid fusion; and (*b*) to have the opposing surfaces of the electrodes large enough.

He uses a 1-amp. arc with a constant voltage of about 25, which corresponds to separation of the electrodes of about 2·8 mm. The electrodes are cut from massive pieces of lead whose opposing surfaces are flat, parallel, and about 2 to 3 sq. cm. in area.

The arc is maintained for only a very short time at a given point. As soon as that point is oxidized the arc is displaced towards the neighbouring regions not yet oxidized, wandering progressively over the whole available surface of the electrodes. Breckpot recommends that the lower electrode should be the negative one.

The photographs are taken by means of a rotating stepped logarithmic sector in front of the slit, and with the sector used a difference of one step corresponds to an increase in time of exposure in the proportion of 1 : 2·5. The curves are drawn with as abscissæ the logarithms of the concentrations, and as ordinates the reciprocals of the times of exposure necessary to obtain equality of density in the photographed images. Such curves are generally linear. The best account of this part of Breckpot's method is given in a later paper (1939).

§ 209. Kaiser (1936) determined tin, antimony, and cadmium in lead alloys using the Feussner spark (§§ 87. 1, *b*, and 135) and a microphotometer. He claims a consistency of ± 2·64 per cent. in determinations of antimony, and less accuracy in those of the other constituents.

Kaiser's paper includes an exhaustive examination of the errors in quantitative determination obtained. The method of working is very fully described.

In this and the other papers of Kaiser (1937*a* and 1937*b*) he states the conditions which he considers necessary to be fulfilled to secure accuracy in quantitative analysis.

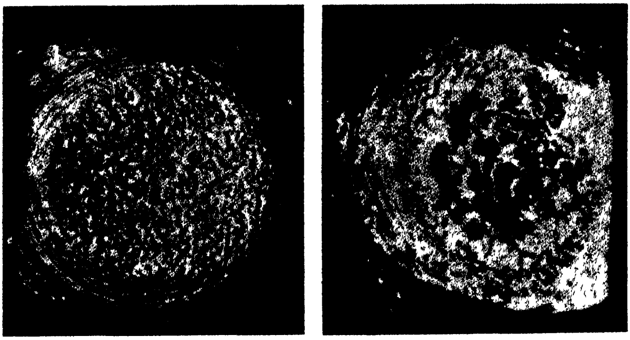
§ 210. Schleicher and Clermont (1931), in one of the first of a series of ten papers appearing in the *Zeitschrift für analytische Chemie* from 1930 to 1937, worked out a system of determining tin in lead. Schleicher prepared standard alloys by melting tin and lead together in a stream of hydrogen, and using the simple spark (§ 87) took spectrograms with the logarithmic sector (§ 121). In the subsequent papers, Schleicher considerably modified his methods.

§ 211. Werner and Rudolf (1938) deal with the determination of arsenic, antimony, bismuth, and tellurium in lead. The paper is of special interest for the investigation of the various sources of error.

Concerning the electrical conditions of the excitation the authors say that a principal source of error is inconstancy of the electrical conditions of excitation. The authors consider that the Feussner spark obviates this variability, and in support of this conclusion they give some interesting photographs showing the appearance of the electrode end faces with correct and with incorrect choice of discharge conditions. They say that in the choice of these conditions the physical properties of the materials of the electrode must be studied, so that the passage of the spark is regular, and the electrodes are equally affected and vaporized over their entire end surfaces. One achieves this through a suitable choice of capacity and inductance in the secondary circuit ; if this is not done films of oxide and slag on the surfaces of the electrodes hinder the passage of the spark and prevent its regular running. Fig. 49

shows the results of what the authors consider the right and the wrong choice of capacity and inductance.

For regularity of discharge they find that both the separation and the form of the electrodes are important. An alteration of the electrode separation alters both the electrical and the thermal conditions between the electrodes ; with the easily fusible alloys of lead even a short sparking causes an increase of the distance by burning, and if neglected is an important source of considerable variations in the analyses. As shown by Badum and Leilich (1937), one can control the constancy of the discharge during exposure by observing the brightness of the spark with a photocell. The authors attain the same object by watching the image of the electrodes.



	A.	B.
Capacity	$\frac{2}{5}$	Full.
Inductance	$\frac{1}{10}$	Full.

Fig. 49.—Effect of Discharge Conditions on the Electrode Surface (Lead).

Since the potential gradient of the spark in the direction of the discharge is not uniform, the condition of the metal atoms varies from the surface of one electrode to that of the other, and the spark lines which are emitted from the ionized metal atoms are found in the places of high potential gradient—*i.e.* near the electrodes. The emission of the arc lines is almost equal throughout the entire distance ; it is for this reason important always to use the middle part of the spark, an image of which is isolated by means of a diaphragm on which an image of the spark is thrown. The arrangement is shown in Fig. 50, and the result produced in the images of the lines is shown in Fig. 51.

By investigation of various sources of error, it was further established by the authors that the width of the slit has an effect on the differences of blackening, and they prefer to work with a broad spectrograph slit, namely, about 0·05 mm. With spectra rich in lines this in many cases is not possible, and the slit must then be narrowed. For quantitative investigation of steel and iron, one usually uses (they say) a slit width of about 0·02 mm. With the lead alloys in question the authors recommend that the slit width should be not less than 0·03 mm., which is easily possible, since the spectra of these alloys are not very rich in lines.

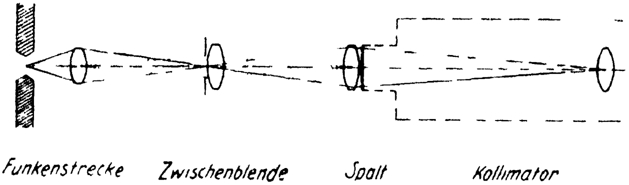


Fig. 50.—Condenser System for using Middle Part of Spark.

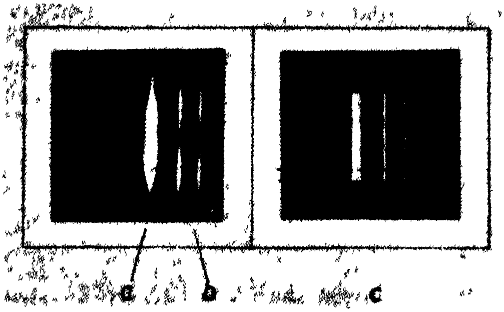


Fig. 51.—Arc and Spark Lines (a, b) without, (c) with, Intermediate Diaphragm.

MAGNESIUM AND ITS ALLOYS.

Pure Magnesium.

§ 212. The magnesium arc requires care in running, or else, of course, the magnesium may ignite. Fortunately, it seems sufficient to establish the purity by the use of the spark for such impurities as are of industrial interest.

The same sparking conditions should be used for the examination of pure magnesium as those indicated *below*, including the auxiliary sparking gap.

Recommended Technique for Magnesium Alloys.

§ 213. Owing to the fact that the magnesium spectrum has few lines, a difficulty presents itself in spectrochemical analysis of its alloys, it being impossible to find line pairs, consisting of a magnesium line on the one hand and a line of the alloying substance on the other, which are sufficiently near in intensity to lie within a satisfactory blackening range of the photographic plate.

Take, for example, the magnesium alloys of the "Elektron" type, containing aluminium 4 to 10, zinc 0 to 1·0, manganese, iron, and silicon up to about 0·3 per cent.: two photographs at least are required if the ordinary spark be used.

It has been found in my laboratory, however, that if one adds a second auxiliary spark gap of greater length, the fainter lines, which are of a higher degree of ionization, are intensified. This simple arrangement, which we call the "tandem" spark, puts a fresh complexion on the analysis of alloys of this type, and also provides a further simple way of controlling the properties of the spark in addition to the customary capacity and inductance (Zehden, 1940).

The following are details of the technique recommended for magnesium alloys of this type, using the standard sparking circuit:

Spectrograph . . .	Medium quartz.
Slit width . . .	0·025 mm.
Condensing lens . .	Type (*ii*), § 54.
Voltage	15,000.
Capacity	0·005 μf.
Inductance . . .	0·25 mh.
Spark gap . . .	3 mm.
Diameter of the electrode sparking surface . .	5 mm. with flat filed ends.
Presparking time . .	20 sec.
Exposure . . .	45 sec.
Plates	Ilford "Ordinary."
Development . . .	2½ min. in standard MQ at 67° F. (19·4° C.).
Auxiliary spark gap .	5 mm.
Magnesium line . .	3074 A.
Other line of pair . .	Iron 2382 A.
	Silicon 2516 A.
	Aluminium 2568 A.
	Manganese 2610 A.
	Copper 3274 A.
	Zinc 3282 A.

§ 214. The difficulty referred to *above* (§ 213), due to paucity of lines in the magnesium spectrum, has been widely appreciated by those interested in this class of alloys.

Whalley (1937), pointing out that the spectrum of magnesium does not contain a sufficient number of lines suitable for use as internal standards, employed a composite spark, a spark, namely, between an electrode of the magnesium alloy under test and one of pure nickel. With the following sparking circuit :

Condenser 0·005 μf., Inductance 0·25 mh., Spark gap 5 mm.,

he found that the pairs of lines Mg 2942 : Ni 2944 and Mg 2911 : Ni 3012 on the photograph appeared of equal intensity to the eye, and these equalities served as a check on the reproducibility of conditions. In about 5 per cent. of the exposures taken in analysis this equality was not maintained, and these exposures were consequently ignored.

Whalley's paper gives a table of lines of impurities which equal the intensity of selected nickel lines at various percentages of the impurities, and the method suffices for the semi-quantitative analysis of magnesium alloys for aluminium, zinc, manganese, and copper.

An alternative method which might be applied is that of the auxiliary spectrum (§ 119).

§ 215. Owens and Hess (1935) apply spectrographic analysis to magnesium-base alloys containing approximately 90 per cent. of magnesium together with varying amounts of manganese, silicon, aluminium, zinc, copper, iron, cadmium, and tin either as alloying constituents or as impurities. The necessity of a frequent check on these constituents in the alloy manufacture makes this problem particularly suitable for attack by the spectrographic method.

The general method of analysis is described, manganese and silicon being used as specific examples. Routine analyses have been developed by the authors for manganese in the range from 0·009 to 1·5 per cent., and for silicon in the range from 0·005 to 2·0 per cent., to an accuracy equal to that of routine chemical analysis.

A condensed spark discharge between solid alloy electrodes is used for the excitation of the spectrum. The mechanical and electrical conditions of the spark are controlled in accordance with a predetermined constant state. The length of the spark gap is maintained at 5 mm. between electrodes of 11 mm. by 3 mm. cross-section. A 1-kva., 110 to 25,000 v. transformer furnishes the spark voltage. In series with the spark gap is an air-core inductance of 0·00003 H. ; in parallel with the gap is a capacity of 0·00577 μf.

The condensed spark under these controlled conditions was found to yield more accurate analyses of magnesium alloys than an arc between solid electrodes. Even when the electrodes are held in massive, water-cooled holders, the burning thereof prevents the maintenance of an arc of constant spectral characteristics.

No lens is used between the spark source and the slit, the source being placed at a sufficient distance from the slit to ensure that all the light from the source which passes through the slit also passes through the spectrograph lens.

The authors found that the maintenance of the spark discharge for a minimum time-interval of 6 min. before exposure greatly increased the accuracy of the analysis.

The authors say that spectral lines chosen for use in the analysis should fulfil the following conditions :

(1) The lines chosen should give suitable blackening over the ranges of the elements occurring in the analyses, and should lie in a wavelength region of constant, or only slightly varying, contrast of the photographic plate.

(2) Whenever possible, only lines of the same character should be compared ; that is, arc lines with arc lines, and spark lines with spark lines. The spectral lines chosen were :

Magnesium . .	2915·5 and 3074·1 A. (both spark lines).
Manganese . .	2605·7, 2610·2, and 2949·2 A. (all spark lines).
Silicon . .	2516·1 and 2881·6 A. (both arc lines).

An analysis may be made by the use of one pair of lines, one of magnesium and the other of the element under test. The use of another pair of lines serves as a check of the analysis.

It has frequently been found by different investigators that the presence of other elements in the specimen markedly affects the spectrographic analysis for the element under test. No such effect was found by Owens and Hess in their investigation. The maximum concentrations of the other elements present in the Dowmetal alloys have no effect upon the analyses for manganese and silicon, thus making possible the use of the same analytical curves for the analyses of the various Dowmetal alloys.

§ 216. Wwedjenski and Mandelstam (1936) use a two-prism "visual" spectrometer with a polarization photometer. They point out that the method of homologous line pairs cannot be applied owing to the dearth of lines in the magnesium spectrum, and get over the difficulty by the use of stepped spectra.

§ 216.1. Beerwald (1939) deals with the estimation of small quantities of beryllium in magnesium alloys (see also § 171.1).

NICKEL.

§ 217. Pure Nickel.—For the determination of impurities in high-purity nickel, a medium quartz spectrograph is suitable, using the simple arc.

For example, in a comprehensive examination of a very pure specimen of nickel, a chemical analysis conducted by proved known methods, but with corrections made, as necessary, by spectrographic examination of the precipitates, gave the following results:

The final chemical analysis by the research chemist at the works was

	Per cent.		Per cent.
Nickel .	99·971	Carbon .	0·010
Iron . .	0·018	Silicon .	0·001

Calcium, chromium, cobalt, copper, magnesium, and manganese were chemically absent.

Spectrographic examination, however, revealed also traces of calcium, chromium, cobalt, copper, magnesium, and lead. Subsequently a full investigation, both chemical and spectrographic, was made as follows:

Six electrodes were taken at random from the parcel and, after pickling in dilute sulphuric acid overnight to remove surface impurities, were submitted to spectrographic analysis by the arc method, using a medium quartz spectrograph.

Comparison spectra, using suitable quantities of the elements deposited on the electrodes, were photographed in juxtaposition to those of the simple electrodes, in the cases of

aluminium,
barium,
beryllium,
bismuth,
boron,
calcium,
carbon,
chromium,
cobalt,
copper,
gallium,
iron,
lead,
magnesium,
manganese,
molybdenum,
phosphorus,
silicon,
silver,
tin,
titanium,
tungsten,
vanadium,
zinc.

The results of the whole analysis were as follows:

	Per cent.
Iron	0·018
Carbon (as *above*)	0·01
Silicon	0·0005
Copper	0·0004
Lead	0·0004
Tin	0·0003
Aluminium	0·0001
Calcium	0·0001
Magnesium	0·0001
Zinc	0·0001
Cobalt	Trace.
Boron	Minute trace.
Manganese	Minute trace.
Sodium	Minute trace.
Vanadium	Minute trace.
Nickel, by difference	99·97

(Hilger, 1940*a*.)

§ 218. In another laboratory (that of the War Department Chemist, Royal Arsenal, Woolwich) commercial nickel is examined for the determination of the following:

	Per cent.
Arsenic	0·01 to 0·05
Cobalt	0·01 to 0·1
Copper	0·01 to 0·1
Lead	0·01 to 0·1
Manganese	0·01 to 0·1
Silicon	0·01 to 0·05

§ 219. Nickel Analysis in connection with Electrolytic Nickel-refining.—Van Someren (1936) describes an investigation to ascertain how far a quartz spectrograph of medium dispersion* could replace chemical analysis for the control of the purity of the nickel. The metals estimated were copper, lead, arsenic, and antimony.

Owing to the complexity of the nickel spectrum, it was found necessary to eliminate the nickel as far as possible. To a solution of the nickel as sulphate other metallic salts were added in known amounts, and the mixed sulphides were precipitated in slightly acid solution. Spectra were recorded from these precipitates in an arc, and the densities of the impurity lines relative to those of the added elements were made the basis for an approximate quantitative analysis.

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* Van Someren's account rather leads one to think that a large spectrograph would have been better.

Some preliminary tests on the arc between metallic nickel electrodes showed that, although 0·0005 per cent. of lead or copper could be detected, the most sensitive lines of arsenic and antimony are masked by nickel lines. The globule technique described by Milbourn (1934) was also tried ; the arc between a globule of the nickel to be tested and a rod of H.S. pure nickel gave the maximum sensitivity to impurities when the globule was positive.

Electrodeposited nickel is not usually homogeneous with respect to the metallic impurities ; to overcome this metallic samples may be converted into neutral sulphate solutions of known concentration, 50 or 100 g. of nickel per litre. Most of the samples tested consisted of solutions of nickel sulphate for use as an electrolyte in the refining of nickel which also contained sodium, magnesium, calcium, and cobalt. The copper, lead, arsenic, and antimony were present in concentrations of only a few milligrams per litre ; larger quantities were added as solutions of salts of these metals.

The modified internal-standard method described by Slavin (1933) was used.

After a number of trials with tin-sulphide, barium-sulphate, and aluminium-hydroxide precipitations, it was found that the best results were obtained from cadmium sulphide containing a little tin. The tin was necessary because cadmium has a rather simple spectrum and does not give faint lines conveniently situated for comparison with the most sensitive lines of the impurities sought. The precipitates were dried and packed in a conical hollow in the lower (negative) of a pair of graphite electrodes. Before using the rod again for a fresh test, the crater was filed away and a fresh hollow made in clean material.

By varying the size and shape of the electrodes, the current in the arc, the quantity of material tested, and the exposure time, a set of conditions was found which gave reasonably reproducible spectra from the cadmium-sulphide powders.

At first weighed quantities of powder were used for each test ; later it was found that the quantity of powder could be judged accurately enough from the depth to which the crater was filled. Each exposure was made with two chargings of the electrode, because better uniformity of the spectra was obtained in that way than by using a larger portion of sample and longer exposure, or by attempting to consume the sample completely during a long exposure.

§ 220. The accuracy attainable by this method is largely a function of the patience and experience of the operator. Some error may arise from efforts to interpolate between the concentrations at which line-equalities occur. This may be eliminated by suitably altering the quantity of cadmium-tin mixture added to the solution and making a fresh precipitate.

The matching of the lines is facilitated by the fact that those chosen are always close together, and that the lines likely to interfere have been noted ; the errors from this source are negligible compared with the errors due to irregularity of arcing.

The most serious source of error is the irregular nature of the arc when metallic salts are placed on graphite electrodes. This error is minimized by the technique described, and in this author's hands produced errors of the order of ± 20 per cent. of the concentration.

The error introduced by the method of chemical preconcentration will be similar to that occurring in the ordinary chemical analysis for minor constituents of an alloy (say 0·5 to 5·0 per cent.), rather than to the much larger errors likely to arise when quantities such as 5 mg. per litre are being evaluated by ordinary chemical analysis.

Nickel Alloys.—Wolfe (1935) used the Duffendack method for determining aluminium in nickel alloys.

THE PLATINUM METALS.

§ 221. Stauss (1935) points out that the high value of platinum makes small lots of metal important commercially, and leads to the careful recovery of all forms of scrap from all sources. The purchase of scrap from any source in turn requires the maintenance of an assay laboratory ready to analyse any material sent in for refining. The chemical inertness of the platinum-group metals has made infeasible the development for spectrographic analysis of methods requiring solutions. The inability to use standard solutions means that quantitative analysis requires standard alloys. The obvious difficulties associated with maintaining a set of standard alloys of the precious metals of sufficiently fine gradation of composition to be useful have acted as a deterrent upon the adoption of quantitative spectrographic analysis, and have led to confining analyses to those of a qualitative or of a semi-quantitative nature, that is, to analyses in which the order of the amount of impurity is determined. The uses of the spectrograph have been, therefore, in those fields in which it is superior because of its speed, its thoroughness, or its modest demands for samples. They fall roughly into three categories :

(1) Identification of alloys.

(2) Special analyses for minor impurities.

(3) Control of the purity of platinum and its alloys for special purposes.

§ 221. 1. Two of the important characteristics of the platinum industry are the large numbers of alloys in use, most of them of minor importance, and the many users to whom platinum and all its alloys are indiscriminately "platinum." From time to time it is necessary to duplicate a sample of metal called "platinum" that is obviously not platinum. Because of the time and cost involved, such a sample frequently cannot be submitted to chemical analysis, and instead, an attempt is made to identify the alloy from its use and its physical properties, such as thermal electromotive force, resistance, and hardness. Where such tests are not possible, or are not conclusive, spectrographic analysis is used. Spectrographic analysis and the measurement of some physical property are usually sufficient to identify standard alloys.

§ 221. 2. The demand for special qualitative analyses for minor impurities comes from two sources : There is the metal returned by the trade because of unsatisfactory service ; this is examined for contaminations. There is also the eternal question within the works of minor impurities, a question which becomes quite acute when nearly unworkable alloys are being made. So far as returned ware, largely laboratory ware or thermocouples, is concerned, the difficulties usually arise from overdoing a good thing. Platinum and its alloys are inert to many chemical reactions, and to many combinations of chemical reactions and high temperatures where other metals fail. In many cases they are used with compounds of metals and metalloids which are safe, while the metals and metalloids themselves are dangerous because they form relatively low-fusing alloys with platinum. In such cases reducing conditions occasionally occur accidentally and a low-melting alloy is formed. When this type of failure cannot be definitely recognized by the user, spectrographic analysis of the area of failure is made to determine whether contamination has occurred. Arsenic, silicon, and phosphorus have been found to cause the most trouble with laboratory ware. In much the same way thermocouples are occasionally contaminated under reducing conditions.

The second need for qualitative analyses arises within the works. The refining of the platinum-group metals is difficult; many of the alloys used are very difficult to work ; many of the products are subject to close specifications in thermal electromotive force, hardness, or resistance ; and the high temperatures of melting and annealing make the question of contamination during working very real. When trouble does occur, it is very difficult to establish the exact origin, and the spectrograph has won a place as an independent judge in such cases. Either it readily establishes and identifies contaminations, or it disproves the theory of contamination. Moreover, it is usually able to locate the origin of the contamination. The spectrograph is useful in testing platinum, rhodium, and iridium sponges, and in examining metal after nearly every stage of manufacture. The importance of this use, the author says, can hardly be overestimated, because it plays so large a rôle in guiding refining and manufacturing operations.

§ 222. Rollwagen and Ruthardt (1936) point out that both qualitative and quantitative analyses of platinum are now so developed that they can easily be employed for any industrial use, and on this account these authors considered it desirable to apply the spectrochemical method also to some of the non-metals. Those of principal importance in platinum are phosphorus, arsenic, and sulphur, since these substances, even in very slight concentrations, have deleterious effects of various kinds. For example, platinum alloys with even so little as 0·005 per cent. of phosphorus show a very objectionable hot-shortness.

The authors found arsenic to be the easiest to deal with, as might be expected, since this substance is always regarded as one presenting no special difficulties. With the condensed spark the arsenic can be clearly distinguished when present to the amount of 0·05 per cent. The most suitable arsenic line is 2349·8 A, as 2881·1 is coincident with a platinum line and therefore unsuitable, while 2780·2 is somewhat less sensitive than 2349·8.

The determination of phosphorus is more difficult, yet in the condensed spark the phosphorus line 2535·7 A. was distinctly present with 0·1 per cent. of phosphorus, while the next most sensitive line, 2553 A., was also just visible. An increase of sensitiveness is given by the interrupted arc, but the ordinary continuous arc with a current of 12 amp. and 110 v. is still better. With this, considerably less than 0·005 per cent. of phosphorus can be seen. However, this kind of electric discharge is too uncontrollable and very unsuitable for thin wires and foil, because of the strong heating. The authors, therefore, sought a method intermediate between the interrupted and the continuous arc. They slowed down the speed of interruption of the arc to about two per second using a current of about 10 amp. at 110 v., or with very thin wires to an even lower value. With this arrangement it was easily possible, with platinum alloys which were no longer "hot-short," that is, which must have contained less than 0·005 per cent. of phosphorus, to distinguish the presence of the phosphorus by the lines 2536 and 2552 A.

The above methods are of no use for the detection of sulphur except if it be present in relatively great concentration, yet it is desirable to be able to detect sulphur in platinum when present to the extent of only 0·05 per cent. Attempts to detect sulphur in various flame spectra were without result. Following an investigation of Goldstein, a vacuum tube was developed, the final form of which is fully described in the paper. The sulphur lines appear in the vacuum-tube discharge. The tube is of quartz, which permits photographs to be taken in the ultra-violet ; this has also the great advantage that traces of the sulphur can be removed from the tube by heating, and this is found to be the quickest way of cleaning the tube. The tube is exhausted with a small diffusion pump. Using a pressure of 10^{-2} to 10^{-3} mm. of mercury, detection of sulphur could be made down to 0·01 per cent. The exposures were of from 10 to 20 min.

RADIUM.

§ 223. Gerlach and Riedl (1934) determined barium, using the interrupted arc (§ 83) with copper electrodes, and putting a drop of solution on the lower electrode—a method much used by Judd Lewis with the ordinary arc. Semi-quantitative results were obtained by comparison with solutions of known strength used in the same way.

Radium accumulates in the barium separated from the residues in the treatment of pitchblende, and the radium and barium chlorides are separated by a long series of fractional crystallizations.

SILVER.

§ 224. Baiersdorf (1934) finds that cadmium can be detected in a concentration of less than 10^{-4} in the spark, 10^{-6} in the interrupted arc (§ 83), and 10^{-7} in the ordinary arc between silver electrodes; palladium to less than 10^{-6} by a special method. The spark was from an induction coil with Wehnelt interrupter similar to that used by Späth (1932).

Determinations were made by comparison with standard alloys of silver and cadmium (concentration: 10^{-2} to 10^{-8}) and of silver and palladium (concentration: 10^{-2} to 10^{-6}).

TIN.

§ 225. D. M. Smith (1936) deals with the spectrochemical analysis of tin. The report is divided into four sections, of which Section 1 gives a very complete summary of previously published work on the spectrographic analysis of tin; while Section 2 deals with the determination of aluminium, cadmium, and zinc present as impurities in tin to 1 per cent. or less, and describes the preparation of synthetic standard alloys. The technique of the spectrochemical determination is fully described. The semi-quantitative method is that of the simple internal standard, and tables are included. This method gives sufficient quantitative accuracy for the purpose required. The method employed was the globule method using a graphite arc.

Section 3 deals with the determination of impurities in tin by means of spark spectra, and contains a revision of his previously published technique for the determination of antimony, bismuth, copper, lead, and silver. Tables are given for all these metals.

Section 4 consists of a general summary and conclusions.

§ 225. 1. Kringstad (1935) gives the technique for determining the lead contents of various qualities of tin plate, with comparisons of the spectrographic and chemical tests.

ZINC AND ZINC-BASE ALLOYS.

High-purity Zinc.

§ 226. The purest zinc of which I have personal knowledge was prepared by the National Smelting Company, Avonmouth, for research work (Hilger, 1940*c*).

The supply was in the form of rods 6 mm. in diameter and 15 cm. long; the rods were cast in graphite moulds.

By reason of their exceptional purity, no chemical analysis was practicable. Although this material can be produced in batches of several lb., the preparation is entirely a laboratory operation, involving repeated distillations under carefully controlled conditions, necessitating skilled supervision.

The method of spectrographic test was to strike an arc between two of the rods, the current across the gap being 3·4 amp. at 28 v.; the exposure was 60 sec. A medium quartz spectrograph was used, and a sphero-cylindrical condenser focussed the light on the slit.

The spectrograms so produced indicated that the metal was almost entirely pure, the only suggestions of impurity being given in Table XXI.

TABLE XXI.—IMPURITIES IN HIGH-PURITY ZINC.

Element	Remarks.	Lines in Evidence A
Calcium . .	Very slight trace in only one strong spectrum.	4226·731 3968·47 3933·67
Copper . .	Very slight trace at most. . . .	3247·550 only
Magnesium .	Minute trace, barely indicated in one spectrum only.	*Raie ultime* 2852·13 only

Elements sought in the spectra described in Table XXI with negative result:

aluminium,
antimony,
arsenic,
barium,
beryllium,
bismuth,
boron,
cadmium,
chromium,
cobalt,
gallium,
indium,
iron,
lead,
lithium,
manganese,
molybdenum,
nickel,
potassium,
silicon,
silver,
sodium,*
strontium,
thallium,
tin,
titanium,
tungsten,
vanadium.

An earlier supply (1931) by the New Jersey Zinc Company, only a little less pure, also prepared by repeated distillation, was finally melted in a fused silica vessel all in one batch, and cast in glass.

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* But the principal lines are masked by zinc.

§ 227. Works Control of High-grade Zinc by the National Smelting Company.—For the analysis of zinc and its alloys a medium quartz spectrograph is used. Spectrographic equipment may be regarded as an essential part of the plant necessary for the production of high-grade zinc, having a purity of, say, 99·99+ per cent. with a tolerance of 0·003 per cent. for each of the impurities lead, cadmium, and iron.

For control purposes two methods are in use by the company at Avonmouth :

(1) *Semi-quantitative* : *for rapid plant control.*—The sample, received in granulated form, is first carefully remelted at a minimum temperature and cast into Pyrex glass tubes 5 mm. in diameter. The rods are withdrawn and broken into two, each portion forming one of the two electrodes. Comparison is then made between the sample electrodes and the standard electrodes containing the impurities lead, cadmium, and iron at the maximum tolerance. Arc excitation under controlled and standardized conditions is employed. This method is extremely rapid and has been found quite reliable. Full quantitative results are obtained by a somewhat longer method, and any samples which show impurity contents approaching the maximum are further examined by the following method.

(2) *Fully quantitative* : *for final examination.*—In this method, devised by Nitchie (1929), the samples are taken up in acid in such quantities that the metal : solution ratio is strictly controlled. Measured small quantities are transferred to hollowed graphite electrodes, which are then dried. Examination is again by arc excitation, against known solution standards prepared under strictly comparable conditions (see also § 233).

§ 228. Sullivan (1936), using a grating spectrograph, placed the sample to be examined in a hole in the lower (positive) electrode of a graphite arc. The graphite electrodes used were ¼ in. in diameter. The lower electrode was drilled with a $\frac{1}{32}$-in. drill to a depth of ¼ in., and the sample under investigation stuffed into this hole.

This author recommends that an inductance should be placed in series with the arc and resistance, in order to stabilize the current, which is important. He prefers to use the sample converted into the form of sulphate owing to the stability of sulphates in the arc, first pointed out by Judd Lewis. After conversion of the metal under test into the sulphate form, by first dissolving the sample in concentrated nitric acid, then adding concentrated sulphuric acid, and finally evaporating the mixture, the residue is dried, ground, and thoroughly mixed.

The author concludes that cadmium and lead can be detected in zinc down to ten parts in one million with an accuracy of 10 to 15 per cent., by use of the logarithmic sector. He considers that percentages of cadmium and lead below 0·001 could also be detected in the graphite arc run as *above*, and the amounts estimated.

§ 229. In a paper by Cyr (1927) comparison is made between the purity of the various commercial grades of zinc, and a description is given of the preparation of the spectroscopically pure metal.

In a paper by Truesdale and Edmunds further particulars are given of the work of H. M. Cyr in producing zinc of spectrographic purity. The paper contains a description of the apparatus for producing the zinc in question, reference to sources of information on physical constants of the purest zinc, and an account of some effects of small amounts of other metals on the properties of zinc.

Technique recommended for Zinc-base Alloys.

§ 230. Twyman and Hitchen (1931) first drew attention to the effect of the variations of one constituent on the intensity of lines of another.

Zinc-base alloys present such variations to a quite unusual degree. For example, an important class of zinc-base alloys contains the same three alloying elements—copper, aluminium, and magnesium—but in amounts which differ in the various alloys. In various " Mazak " alloys, for instance, we have

Aluminium . . .	About 4 per cent.
Copper . . .	Varying from 0 to 3 per cent.
Magnesium . . .	Varying from 0·03 to 0·04 per cent.

It is found that either of the above differences in the percentage of copper or magnesium affects the intensity of the lines of the other two constituents (see also § 235).

To avoid the plotting and use of a number of graphs (one set at least for each of the separate " Mazak " alloys), an investigation has been carried out in my laboratory whereby it has been found possible to deal with the whole of the " Mazak " alloys with one set of graphs. It must be noted that not only the variation from one type of these alloys to another, but even that between different specimens of the *same* type, sometimes requires these special procedures to be used.

The following technique has been found to yield good results with a minimum of trouble. A medium quartz spectrograph and standard sparking circuit are used :

Condenser	0·005 μf.	Voltage	175 v. A.C.
Self-inductance	0·25 mh.	Current (primary)	1·5 amp.

A new and important modification is introduced—an auxiliary spark gap in series with the electrode spark gap (Zehden, 1940). The auxiliary gap is formed by two rods of copper, each having a flat circular sparking surface of 5-mm. diameter. This arrangement we call the " tandem " spark.

The specimens for analysis and those for preparing the graphs have flat circular sparking surfaces of 5-mm. diameter. These surfaces can either be turned on a lathe or filed. The other conditions are

Spark gap for specimens under analysis	3 mm.	
Auxiliary spark gap	5 mm.	
Slit width	0·025 mm.	
Plate	Ilford " Ordinary."	
Presparking time	20 sec.	
Exposure	30 sec.	
Development	2½ min. in normal-concentration standard gaslight M.Q. developer at 20° C. (68° F.).	
Fixing solution	2 lb. of hyposulphite of soda, 1 oz. of potassium metabisulphite, 1000 ml. of water.	
Zinc line	2583 A.	
Other line of pair	Copper	2370 A. (above 1 per cent. of copper).
	Copper	3247 A. (below 1 per cent. of copper).
	Aluminium	2575 A.
	Magnesium	2852 A.

Preparation and Use of the Graphs.—Owing to the Hitchen effect mentioned *above* the following special procedure must be observed :

Determination of copper. Let D_{Mg}, D_{Zn}, D_{Cu}, D_{Al} indicate the deflections obtained with the microphotometer for the lines of the metal indicated *above* (following the procedure recommended for the use of the microphotometer described in § 68). For the determination of the copper in any of the " Mazak " alloys one set of graphs suffices, but log $(\sqrt[3]{D_{Al} \cdot D^2_{Zn}}/D_{Cu})$ instead of the usual log (D_{Zn}/D_{Cu}) must be plotted against the logarithm of the percentage of copper.

Determination of magnesium. For the determination of the magnesium in any of the " Mazak " alloys, plot log $(\sqrt[3]{D_{Al} \cdot D^2_{Zn}}/D_{Mg})$ instead of log (D_{Zn}/D_{Mg}).

Determination of aluminium. It has not been found possible to evolve an expression for aluminium like those for copper and magnesium, but if the variation of the copper content is small then aluminium can be determined by plotting the usual log (D_{Zn}/D_{Al}) against the logarithm of the percentage of aluminium. If copper varies as much as from 0 to 3 per cent., as in " Mazak " and " Zamak " alloys, then the following special conditions must be observed :

One rod of the sample to be analysed must be sparked against a pure copper rod, with a presparking time of 20 sec. and an exposure of 60 sec., all other conditions being as *above.* By this means the variation due to copper is obviated, and only one standard graph is necessary. Log (D_{Zn}/D_{Al}) is then plotted as usual against the logarithm of the percentage content.

Determination of Impurities.— Lead, iron, and cadmium can all be determined from the same exposures as those taken for copper and magnesium.

§ 231. Other Techniques.—In 1935 the quartz spectrograph (medium size) was already in regular use by the Norske Zinkkompani A/S. in Norway as a method of keeping a daily check on the purity of the electrolytic zinc and cadmium produced. Their outfit has been used for the estimation of magnesium, tin, and other impurities in zinc die-casting alloys, and they have also found it useful in detecting relatively rare elements, such as indium, germanium, thallium, and tin, in zinc ores. Precipitation of mixed sulphides from solutions to which copper has been added, followed by spectrographic examination of the precipitate, has been used for the rough quantitative estimation of germanium in solutions and solids.

§ 232. Breckpot and Körber (1936) extend the method of using copper oxide as a base (§ 138, *b*) to the use of zinc oxide for a like purpose, and give tables for the determination in zinc oxide of

antimony,
arsenic,
bismuth,
cadmium,
copper,
germanium,
indium,
iron,
lead,
magnesium,
nickel,
silver,
thallium,
tin,

using a graphite arc. The stepped sector is used as in the case of Breckpot's work with copper oxide, this being supplemented with a microphotometer. The angular apertures of the sector, being in geometrical progression with a common ratio of approximately 1 : 2·5, are as follows: 3·6°, 9·04°, 22·7°, 57·05°, 142·3°, and 360°—the last value indicating, of course, the part of the slit which lies outside the sector. Each step occupies 1 mm. of the slit.

This paper gives a list of elements which have lines coincident or almost coincident with the weaker lines of the zinc. The most frequent of these coincidences are occasioned by lines of nickel, chromium, manganese, copper, titanium, vanadium, and iron. All these elements, except iron, are rare in zinc, and complications due to these coincidences are therefore not dangerous. The data are, however, useful in cases where one wishes to estimate impurities in blendes, since one can at once tell which lines must be used only with caution.

The photometric method may be described here. One starts by regulating the intensity of the lamp of the microphotometer so as to obtain a standard deflection. One then determines the galvanometer deflections corresponding to three steps of the spectrum, two of which belong to the first line, and the third to the second line, of the pair which are to be compared. If one has several measurements to make in the region where the gamma of the plate is constant, that is to say, between 2500 and 3600 A., one need only measure two steps of a single line, for example a zinc line. A single measurement on the line of each impurity will then permit the determination of the relative intensity. It is essential to take care that the various steps of the lines measured have densities lying within the rectilinear region of the blackening curve. The author states that when he adjusts the microphotometer lamp to give a deflection of 360 mm., the galvanometer deflections must, to fulfil this condition, lie between 35 and 150 mm. in the region from 2500 to 3600 A.

A study of the fluctuations of the graphite-arc spectrum of zinc oxide with variations of current, distance apart of electrodes, and polarity shows that the resonance line 3075·88 A. ought to be rejected as a comparison line, since it is very sensitive to fluctuations of arc intensity, particularly with currents varying between 1 and 5 amp., this change of current causing its intensity relative to that of the neighbouring line Zn 3072·08 to fall from 10 to 0·4. The fluctuations of Zn 3075·88 are still greater in an arc between metallic electrodes, variation of the current from 0·8 to 2 amp. causing the same variation of intensity, from 10 to 0·4. (The reader should here be reminded that in general resonance lines, subject as they are to self-reversal—§ 42—are not satisfactory for quantitative spectrochemical analyses.)

The paper gives tables of lines to be used in the estimation in zinc oxide of the elements mentioned *above*. Breckpot uses these tables in two ways for approximate analysis, firstly by the internal-standard method, and secondly by microphotometric interpolation. Each pair of lines (one of the basis metal and one of the constituent) are of equal intensity at *several* different percentages, according to the steps of the spectrum in which one observes them, and these percentages are set forth in the tables. For more accurate determinations the microphotometer is brought into play for interpolation.

The reader who is interested in Breckpot's method of using the stepped sector should consult Breckpot (1939).

§ 233. Nitchie (1929) describes methods developed in the laboratory of the New Jersey Zinc Company by means of which several hundred analyses were carried out each month, many of them being routine control analyses. The quantitative method adopted, which had been used in the laboratory for many years, was to compare the intensities of the lines of the elements to be determined in the spectrum of the unknown sample with those of the same lines in a graded series of standards of similar composition and photographed under similar conditions. Comparisons between spectrographic analysis and chemical analysis in the determinations of lead, cadmium, tin, and manganese in small percentages show the very satisfactory agreement obtained, the purpose being to control high-grade zinc for small amounts of impurities.

Nitchie prefers the arc for most purposes, although some elements, such as selenium and tellurium in very small amounts, and most of the other non-metals, can best be detected by means of the spark. He prefers carbon electrodes. He lays considerable stress on the choice of a sampling method that will ensure that every portion of the materials whose spectra are registered on the plate shall be as nearly as possible truly representative of the main bulk of the material. The amount of sample necessary for a single determination is ordinarily from 20 to 50 mg. This is much too small an amount to obtain by cutting down the solid material, even in the form of an extremely fine powder, and he therefore finds the safest method is to use solutions.

The method finally adopted in the laboratory of the New Jersey Zinc Company was to dissolve the sample and to adjust the volume of the solution to some simple ratio to the weight of the sample used.

A measured amount, usually 0·1 ml., of this solution is dropped from a capillary pipette into a hole in the upper end of a graphite electrode. A convenient size for the electrodes is 8 mm. in diameter and 50 mm. long. Prior to adding the solution, the electrodes are prepared by burning them for a minute or two in a 6- or 8-amp. arc. This develops a certain amount of porosity, and at the same time helps to expel traces of impurities from the graphite. The electrodes are then cooled before adding the solution, after which the electrode is dried in an oven. The impregnated graphite is used as the lower electrode in the arc, the upper one being also of graphite, arranged to permit air to be drawn through it.

Nitchie uses a large quartz spectrograph, and gives as a rule 3-min. exposures using a 10-amp. arc with a 60-v. drop across the arc terminals. This length of time is sufficient to ensure the complete evaporation of the sample, or at least the expulsion of all the constituents to be determined. It is necessary that none be left in the electrode, otherwise erratic results will be obtained.

§ 234. Winter (1937) determined aluminium, copper, magnesium, and silicon, and the impurities iron, cadmium, and lead in zinc and aluminium alloys, using the spark and the microphotometer. He prepared the electrodes by casting the alloy in a mould. Tests were made by him of the intensity ratio Si : Al for different amounts of presparking, and he also correlated this with the microscopic structure of the surfaces of the electrodes. Uniformity of the intensity ratios Si : Al and Mg : Al was found after one minute, and of Al : Zn after three minutes.

Chill Moulds for casting Electrodes in the Analysis of Zinc Alloys.

§ 235. A paper by Lueg and Wolbank (1939), which deals incidentally with this subject, is worthy of a long abstract because of the many suggestive observations made by the authors, some of which closely coincide with those observations in my laboratory which led to the technique described *above* (§ 230). The authors point out that in the composition of fine zinc alloys it is important that certain impurities should not exceed certain limits. Lead, cadmium, and iron may be mentioned as among these. Spectrochemical analysis is suitable in a particular degree for this kind of analysis, on account of its high sensitivity.

They refer to the methods for the spectrochemical analysis of zinc alloys developed by Winter (see *above*, § 234), and point out that subsequent methods of analysing zinc alloys were based on the work of Wintèr, and improved by making use of the experience obtained in the analysis of aluminium alloys.

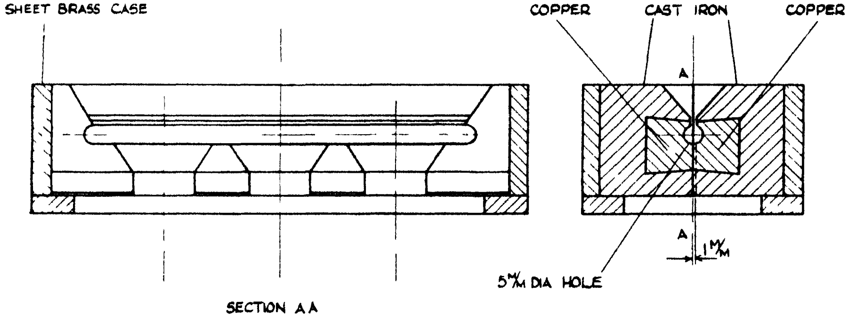

Fig. 52.—Chill Mould for Sparking Electrodes (Lueg and Wolbank).

The technique of Lueg and Wolbank is as follows:

For electrodes, rods of 5-mm. diameter are used, with hemispherical ends. This shape was chosen to avoid the presentation of edges or other features tending to localize the spark.

For making electrodes from a melt, the use of a chill mould is advantageous, as is customary in the analysis of aluminium alloys. The heterogeneity, which can give rise to serious error both with zinc and with aluminium alloys, is so far lessened by the use of suitably chilled castings as to be within the limits of accuracy of the analysis.

The chill mould used by the authors is shown in Fig. 52. The body is of a metal which is a bad conductor of heat (*e.g.* cast iron), while within it is the mould itself, made of copper so as to have high thermal conductivity. The gate is open throughout its entire length, which gives a uniform result. The long gate becomes wider upwards ; thus the mass of metal in the head is great in comparison with that of the test-piece.

The less fusible alloys tend to set during the pouring, and this is to be avoided by warming the mould if necessary. On the other hand, the whole purpose of the design of the mould is to secure quick setting.

Excitation.—The course of the spectrographic analysis is obviously not determined by the mode of producing the test-pieces, and these can also be made from machined or completely finished parts ; when they are in the form of thin sheet they can, after the surfaces have been cleaned, be pressed into spherical shape according to the desired form of electrode.

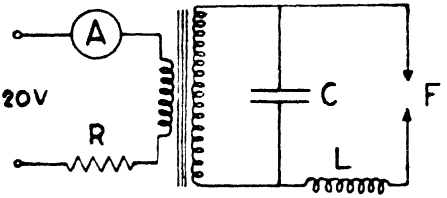

Fig. 53.—Continuous Sparking Circuit.

Use has been made by others of a sparking circuit in which the discharge is either mechanically or electrically interrupted, but the authors use the ordinary resonant circuit (as described in § 87) shown in Fig. 53. The transformer is controlled by a resistance R and ammeter in the usual way. The secondary voltage is stepped up in the proportion of 60 : 1, and there is a condenser C in parallel with the sparking circuit. The circuit between the condenser and the spark has self-induction L which can be varied between 0 and 0·3 mh. With the sparking conditions set forth *below* the condenser is only charged once every half-period up to the discharge voltage.

Analytical Procedure.—One cannot fulfil in a single spectrum the conditions for determination both of the smallest traces and also of the desired constituents, since different exposures are required for these purposes. It is convenient to arrange that the various spectra lie one under another in order of decreasing times of exposure. To produce the graphs one requires the usual series of standard alloys with at least three different proportions of the various constituents.

In calculating the percentages where there are great differences in the proportions of the constituent in the metal to be analysed and in the standard specimen, one must take into account the varying quantity of the basis metal, zinc. The relative intensities of a line of the constituent and a line of the main substance are determined by the proportion of these elements in the alloy. Thus the percentage of the constituent in the standard is to be referred to that of the basis metal, zinc. This relative proportion is calculated according to the formula :

$$R_X = \frac{100x}{G} \text{ per cent.},$$

where x is the absolute percentage of the element in question, and G that of the basis metal.

On the standard curve the relative proportion for the sample is read off. The absolute proportion is then calculated according to the formula :

$$x = \frac{100R_X}{100 + R_X + R_Y} \text{ per cent.}$$

In this formula R_Y represents the sum of the relative proportions of the entire remaining constituents. If R_Y is omitted, the results will have a relative error which is approximately the same as the difference in the percentage proportions of zinc in the alloys in question.

For the determination of aluminium, copper, and magnesium in zinc alloys, the blackening of the following lines is measured : Al 3082 : Zn 3076 A., Mg 2798 : Zn 2801 A., Cu 2545 : Zn 2570 A. The concentration range lies between

Aluminium . . .	2 and 13 per cent.
Copper	0·3 and 3 per cent.
Magnesium . . .	0·01 and 0·1 per cent.

In the determination of magnesium the variation of the aluminium percentage has a great influence on the relative intensity of the spectral lines. This effect is due to the alteration of the intensity of the *zinc* spectrum with increasing aluminium content ; comparison of the magnesium line produced by the same magnesium content with the background resulting from varying proportions of aluminium gives identical differences of blackening.* In the spectrochemical analysis of solutions, too, the effect of the ground spectrum is absent.

Owing to this effect it is necessary to prepare the analyses with standard alloys in which the aluminium content is approximately the same as in the specimens to be analysed. One cannot safely carry out the magnesium determination in a zinc specimen containing 4 per cent. of aluminium, on the basis of a comparison which has been made from a standard alloy having 10 per cent. of aluminium, nor *vice versa*. The impurities of prime importance in zinc-base alloys are lead, cadmium, and iron. The further disturbing impurities thallium, bismuth, and tin are not spectrographically observable in the ordinary quality of fine zinc. If lines of these latter elements appear, injurious proportions may be present; if not, one can be assured that they are not present in amounts that will harm the alloy. For the determination of the former elements the following lines are measured :

Fe 2382 : Zn 2394 A.
Cd 2144 : Zn 2138 A.
Pb 2204 : The background in the neighbourhood of the line (an average of 3 readings should be taken).

Comparison of the lead line is more easily made with the background than with the neighbouring zinc line. The several exposures must, however, be as uniform as possible. It will be observed that in the absence of aluminium the background is a little weaker ; the standard alloys should, therefore, also contain aluminium. The zinc reference line used in determining cadmium shows two maxima as a result of self-reversal, and the authors state that it is the reversed maximum that should be measured. In the analysis of the impurities, a visual comparison of the intensity frequently suffices. The presence of the elements tin, bismuth, and thallium can be detected by the lines Sn 3175, Bi 2898, and Tl 3776 A. respectively.

Since a large proportion of the lines suitable for analysis lie in the extreme ultra-violet, it is desirable to use a plate which has sufficient sensitiveness in this spectral region. The following are other conditions given by the authors for carrying out the analysis :

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* In the determination also of nickel in aluminium alloys this effect is of importance. G. Balz (1938) notes a similar effect also in the determination of zinc in aluminium.

Primary resistance R	90 ohm.
Primary current	1·3 amp. at 220 v.
Self-induction L	$0{\cdot}1 \times 10^6$ cm. (0·1 mh.).
Capacity C	8000 cm. (0·009 μf.).
Separation of electrodes	4 mm.
Slit width	0·03 mm.

For the main analysis :

Presparking time	40 sec.

For the determination of the impurities :

Presparking time	1 min. 20 sec.

With the technique of analysis described *above* it is claimed that aluminium and magnesium and the usual impurities lead, cadmium, and iron can be determined with sufficient exactness. In the determination of copper, however, considerable variations are found. The estimation of iron, if more than 0·1 per cent., is uncertain on account of the irregular distribution of this element (present as $FeZn_7$) in the structure. Also in the analysis of lead, in proportions greater than 1 per cent. there are difficulties consequent on the segregation of the lead.

A test for the standard alloys is found in the principle that the blackening is a linear function of the logarithm of the concentration ; thus where the establishment of the proportions in the standard by chemical analysis is difficult, as, for example, with magnesium, the actual proportion can be established by means of spectrochemical analysis of a solution.

Experiments were carried out with various electrical conditions of excitation in order to avoid the uncertainty in the determination of copper. Improvements can be obtained by raising the energy of the spark discharge, as is found in the analysis of Silumin. The electrical circuit is the same as in Fig. 53, but the following values can be adopted with advantage :

Primary resistance R	60 ohm.
Capacity C	1800 cm. (0·002 μf.).
Self-induction L	1 winding of 60-mm. diameter.

With a separation of the electrodes of about 3 mm. the primary current should be 2·2 amp. For the determination of copper the line pair Cu 3274 : Zn 3076 A. is suitable. Under these conditions, however, the determination of impurities is very difficult, the background as compared with the weak lines being stronger. The detectability of traces is thereby reduced. However, the observation of the upper limits of the objectionable impurities is still possible.

CHAPTER X.

THE ANALYSIS OF SUBSTANCES NOT IN METALLIC FORM, INCLUDING GASES.

§ 236. Introduction.—Ways of dealing with liquids and powders have been given in various places throughout the earlier chapters, but a fuller description will be given here of a few useful techniques. They refer to work quite unconnected with the usual routine of a metallurgical laboratory, but should none the less be of interest to every practical spectroscopist, for anyone engaged in spectrochemical analysis may, on occasion, have to deal with such problems as the metallic contamination of foodstuffs, and the distribution of metals in soils, in plants or in animals feeding thereon, in paints and enamels, not to speak of ores, clays, and other mineral specimens. Many more references and abstracts will be found in Twyman (1938*a*).

§ 237. Judd Lewis Pellet Method (§ 115).—This is applicable to the ashes of organic material, to precipitates, and to powders generally, and is used with arc spectra. It has already been described in Chapter VII, but a few further notes will be of interest.

The sulphation referred to, assisted by the ammonium sulphate, helps greatly to regulate the arcing effect and to ensure constant results. Many years ago Dr. Judd Lewis studied the effects of different acids on the arc spectrum lines of the metallic elements, and found that sulphuric acid produces much the best results, nitric acid poor results, and acetic acid still worse ; whilst phosphoric, boric, and silicic acids have a weakening effect. Hydrochloric acid gives only fair results with the arc, but remains the most advantageous for sparking solutions.

§ 238. Judd Lewis Ratio Quantitative Method.—This is the simplest of all quantitative methods (§ 115). Spectrograms are produced by the pellet method, and the intensities of the lines compared visually with similar pellets of known composition.

The visual observation consists merely in visual comparison of similar spectra taking advantage of the internal-standard principle, and this is very convenient in the laboratory of a consulting chemist, where such problems are of only occasional occurrence, as it avoids the preparation of graphs or any other preliminary. It is one of the most reliable of all methods if a little patience is exercised to produce known and unknown spectra of substantially equal intensity throughout.

A preliminary spectrogram serves as the basis by establishing a qualitative analysis, and on comparison of the intensities of significant lines with the corresponding ones in a standard "ratio powder," first estimations of the quantitative values are made, and may perchance be sufficient for the purpose in view.

A "ratio powder" is composed in the main of a basic element, for example calcium, "medicated" with known proportions (say 1 or 3 per cent., etc.) of certain elements desired, for example lead. Then the intensities of the spectrum lines of the material and those of the ratio powder being equal, the intensities of the lead lines in the two spectrograms may be compared, and then indicate the "ratio" of lead in the unknown to the calcium.

The fundamental principle to be observed is to bring the material under analysis into *a constant condition* (*e.g.* sulphates) and to compare its spectrum with that of a synthetic mixture of similar quantitative composition *in the same condition.*

The principle of "ratio" as here understood appears to be new as a method of reporting results in quantitative spectrochemical analysis. In practice Judd Lewis has found it more satisfactory than any other for the occasional problem, and its appreciation by other workers who have tried it augurs well for its general acceptance. Some of its advantages will be realized in considering, for example, a vegetable ash. Such an ash includes carbonates, chlorides, phosphates, silicates, etc. in unknown proportions, and the percentages of these in the ash will vary more or less according to the method of ashing, etc. On the other hand the ratio of, say, lead, a minor element, to calcium, a major element, will remain constant throughout, both in the original biological material and in its ash, whatever the treatment. The fact that these ratios of the various minor elements to a predominant element have been determined removes the necessity of detailed knowledge of the composition of the ash. It follows that if the percentage of calcium either in the biological material or in the ash is known, the percentage of lead or of any other minor element so determined becomes known.

Spectroscopically pure chemicals in the form of powders are brought into the same condition of chemical combination as the specimens under test, in the case under consideration the sulphated ashes. The chemical substances found in the qualitative analysis are then brought together in a synthesized mixture which is the first rough approximation to a match of the substance under test. If, as is general, there is a predominant element such as calcium, this may be selected as the base and may be medicated with the other elements in any desired ratio. The mixture is formed into a pellet, and comparison spectrograms are taken, adjacent on the same plate, of this first trial and of the pellet under test. From the results of this test a second approximation is made in the same way, and usually on the third or fourth approximation a satisfactory match is obtained, which gives the analysis of the ash under examination. It is convenient to use a pellet, but it should be pointed out that even so small a quantity as a single milligram can be quantitatively determined in this way.

§ 239. Ramage's Method (1929) as improved by Steward and Harrison (1939).—The improvement in Ramage's method referred to originated in an investigation by Steward and Harrison (1939) into the quantitative determination of rubidium in the presence of other ions common in plant extracts. After considering the stannic-chloride method which was used by Fresenius (1931) for the determination of rubidium and cæsium in natural waters, Steward and Harrison came to the conclusion that the estimation by that method of rubidium in plant tissues must be laborious.

The method of Lundegårdh is accurate and satisfactory, but it entails a rather complicated spraying device, and the apparatus contains parts which must be cleaned between operations. Ramage's method can be carried out with much smaller quantities of solution, but was never developed by Ramage to the point where the percentages were evaluated with the aid of the microphotometer. It was the object of Steward and Harrison so to improve the technique that an accuracy comparable with that of Lundegårdh's could be obtained, together with the advantages in simplicity of the Ramage method.

Part of the advantage of Lundegårdh's method depends on the great control of combustion which a gas flame permits, control which is not achievable by the use of an arc. Steward and Harrison therefore used the flame method. The apparatus and method are described in §§ 75 and 139.

The combustion conditions result in the almost complete absence of a continuous spectrum ; special importance is attached to this, since the presence of a variable continuous spectrum complicates comparisons. The fine adjustment of the flow of coal-gas is obtained by a screw-clip or needle-valve, and the oxygen pressure is fixed by a reducing valve set to deliver at 30 lb. By means of these adjustments the flame is made to conform to arbitrary standard dimensions (*e.g.* over-all height, and size of inner cone), which are kept constant throughout each series of combustions. The steady flame which is essential can best be obtained in a draughtless cellar. Even so the flame must be screened (by coloured glass) from the operator's breath, and rapid movements near the flame should be avoided.

§ 240. Combustion Technique.—In the method of Lundegårdh (1929, 1936) either aqueous solutions are introduced into an air-acetylene flame, or spectra are produced from solutions by an "immersion spark apparatus." In the former method a complicated device, which operates with amounts of 1·0 or 5·0 cc., is used, and the apparatus contains parts which must be cleaned between operations. The technique of Steward and Harrison requires only very small amounts of solution, and is so rapid that all the operations for some twenty combustions can be completed in ten to fifteen minutes. The speed of the operations and the absence of all vessels which need cleaning are noteworthy features.

Only aqueous extracts have been analysed. The material entered the flame dried on filter-paper after the method of Ramage (1929), Munktell's Swedish filtering paper No. 00 being used cut into rectangles 3 in. × 0·7 in. One edge was rolled preparatory to forming a spiral, and a known amount of solution from a micro-pipette, calibrated to deliver 0·1, 0·075, 0·05, and 0·025 cc., was run evenly over the middle of the paper. When using amounts greater than 0·05 cc. this operation was performed in stages with periodic drying over a small flame or hot-plate. The dry papers were then rolled spirally into a tight spill, at each extremity of which was a region free from the dried sample. To prevent the spiral from unwinding one end was flattened and twisted through 90°. Only those papers which were uniform in length and tightness were used, and before combustion the papers were thoroughly dried in a vacuum oven.

Especial care was taken to ensure that all papers were burned in the same manner and in the same part of the flame. This was finally accomplished by the use of an apparatus designed for the purpose. This consisted of three essential units: an asbestos screen, the burner with its ebonite mount and heavy stand, and the unit which carries the paper spill.

The screen is placed between the flame and the spectrograph (Fig. 23), so that only the light which passes through a wide slit reaches the spectrograph. The best position for the screen is easily found by trial. It should be high enough to screen out the direct light from the small luminous flame at the seat of the combustion and yet low enough to permit sufficient sensitivity to be obtained. The arrangement shown in Fig. 23 was satisfactory, and the spectrograms obtained were almost completely free from continuous spectrum.

Both the silica burner and the paper spill are carried on heavy rigid mounts attached to saddles S_1, S_2 which can slide along a rigid, triangular, optical bench-bar, to which they can be locked at will. The optical bench is precisely aligned with the spectrograph, and the technique depends upon the strict alignment of the paper spill, the flame, and the slit throughout the combustion.

The paper spill is held by a clip with jaws made to hold the flattened end (see plan on *AA* and view on *B*, Fig. 23). The clip is rigidly fixed to a shaft, which in turn is clamped to a centre post mounted on a small platform. For any given position of S_2 the shaft and paper spill can be moved smoothly and horizontally along the axis of the bar for a distance somewhat greater than the length of the spill. To attach the spill the saddle S_2 is withdrawn to a convenient position defined by a stop. The paper is correctly aligned by means of the indicator (see vertical section, end elevation, and plan on *AA*, Fig. 23), the tip of which, in its forward position, denotes a point near to the flame, in alignment with the shaft and in the vertical plane of the centre tube of the burner and the slit of the spectrograph. The alignment indicator is withdrawn before the combustion begins. The passage of the paper into the flame is controlled by the wheel W_1, which operates the rack and pinion R_1. The height at which combustion occurs can be varied at will by the coarse rack and pinion W_2, R_2, and a vertical adjustment of the burner can also be made when so desired.

The flame has an outer and colder zone, within which is a sharply defined, hot, inner region at the edge of the oxygen cone. The saddle S_2 is moved along the bar rapidly from its first position until the tip of the spill reaches the hot zone of the flame; then, by means of the wheel W_1, the approach of the spill can be so regulated that its brightly glowing tip, which is kept under observation through coloured glass, remains at the edge of the oxygen cone. In other words, the paper burns as quickly as it enters the flame, which should be neither so fast that it projects into the interior of the oxygen cone, nor so slow that combustion occurs in the outer and colder zone.

With this apparatus it was not found necessary to introduce an internal standard, the conditions observed being sufficient to ensure reproducibility of results.

§ 241. Limitations of the Method.—The combustion technique, using identical standards, produced lines which were not visibly different, although the eye can just detect 5 per cent. differences in the intensity of the lines. The microphotometer showed that variations did, however, occur. Four replicate determinations from 0·1 cc. of 0·0024 M. solution yielded deflections on a given plate of 8·7, 8·8, 8·6, and 8·5, using the line Rb 4215·6 A. The maximum deviation between the quadruplicate determinations correspond to a concentration difference of 0·00012 M., or a spread of 5 per cent. and a maximum difference between a single observation and the mean of 2·5 per cent.

Difficulties still remain in the use of dried, ground tissue samples. The method described when applied to solid samples does not result in precise combustion. The intensity of the lines produced by known amounts of rubidium contained in dry samples was greater than that of the lines from the same amount of rubidium free from any plant material. It was found that even sugar added to the rubidium solution increased the intensity of the lines, and since the diluted water extracts contained some soluble organic matter, the possibility that this caused an increase was investigated. Three replicate determinations of 0·1 cc. of 0·0024 M. rubidium gave deflection readings of 8·2, 8·1, and 8·0, while the same amount added to and re-extracted from potato discs and dissolved in the quantity of water originally present in the tissue gave the deflection readings 8·5, 8·5, and 8·6. These differences due to the soluble matter in the water extracts correspond to a difference between the mean concentrations of 0·00016 M. in the estimation of 0·0024 M., or 6·7 per cent. Though greater than the error of determination, this factor can be eliminated, if necessary, by preparing the standard rubidium solutions in water extracts of tissue. The presence of unusually high concentrations of potassium also increased the intensity of the lines produced by a known amount of rubidium. This effect was only of the order of

5 per cent. when potassium of strength 1·0 M. was added to a rubidium solution of concentration 0·008 M.

On pure solutions, using replicate determinations, the method is capable of an accuracy of the order of 2·5 per cent. On the potato-tissue extracts used in this work the error of the mean of replicate determinations need not exceed 5 per cent. This accuracy was adequate for the purpose of the experiments here described.

§ 242. **Application to Other Elements.**—The technique described has obvious applications to any elements which can be extracted by hot water and give suitable lines in the flame spectra. Using the same method the other alkali metals also can be determined, and the authors have applied it to the determination of lithium and cæsium. In the case of potassium the lines 4047·2 and 4044·2 A. were used, and for amounts of 0·1 cc. and the combustion procedure already described the sensitive range fell within the limits 0·05 M. and 0·005 M. for Ilford process plates.

THE SPECTROCHEMICAL ANALYSIS OF GASES.

§ **243.** Spectrochemical analysis is not, in general, of the same value in the analysis of gases as of metals, although there are many instances in which the spectrographic method can be used to advantage. The analytical problems met with are so diverse that it is not possible to give any detailed general account of the method to be adopted. For example, gases in any of the following categories may occur:

(1) Elementary gases which give their own characteristic line or band spectra, *e.g.* hydrogen, neon, nitrogen.

(2) Compound gases which give their own characteristic band spectra, but which may be dissociated by the excitation process to give band spectra of other compounds or the characteristic spectra of their constituent elements, *e.g.* water vapour, oxides of carbon.

(3) Elementary gases which can be detected by the characteristic spectra of certain of their compounds, *e.g.* fluorine.

(4) Compound gases which can be detected by their molecular absorption spectra, *e.g.* carbon dioxide.

§ **244. Excitation of Spectrum.**—In almost all cases it is necessary to have the gas present in, or capable of being transferred to, a suitable vessel in which its spectrum can be excited. This may take the form of a spectrum tube with sealed-in electrodes, in which case an electric discharge can be passed through the gas or a spark passed between the electrodes. If the gas is in a vessel not provided with electrodes, the spectrum may be excited by a Tesla coil or by an external H.F. oscillator.

A number of precautions must be taken, especially in the case of quantitative work, in order to obtain reliable results :

(*a*) Special care must be taken to remove occluded gases from the inside of the walls and from the electrodes of the tube before filling with the sample under examination.

(*b*) The gas pressure in the tube and the conditions of excitation must be carefully controlled, as the ratio of the line intensities of two components of a mixture may vary with pressure, even though the two gases are present in the same proportions.

(*c*) The rate of clean-up in the electric discharge varies with the nature of the gas, so that the apparent proportions of the gases in a sample may change with the time of running of the discharge. The time of running of the discharge before observation of the spectrum and the time of exposure must therefore be controlled.

(*d*) The ratio of line intensities of two components of a gas mixture may be affected by the presence of a third gas. Measures must therefore be taken to avoid effects due to variable concentration of a third constituent.

The remainder of this section will be devoted to an account of a number of typical investigations which should serve to illustrate the various methods used. The examples given have been divided into four groups corresponding to the classification given in § 243.

§ 245. Group (1).—Moureu and Lepape (1922) have described methods for determining the quantity of krypton or xenon in gases by adding argon for use as an internal standard. Limits are given between which the intensity of the lines varies linearly with the amount present.

Günther and Paneth (1935) have applied the spectroscope to micro-analysis, and have found that, in quantities of helium not greater than 10^{-7} cc., hydrogen must amount to 0·1 and neon to 0·002 per cent. to be detected.

Van Liempt and Visser (1934) have used the spectrochemical method to detect argon in argon-nitrogen mixtures.

Klauer (1934) has discussed the most suitable method of excitation for analytical work, and concludes that the H.F. glow discharge produced by a Tesla coil and applied to external metal-foil electrodes around the tube is to be preferred. Study of various gas mixtures gave the following limits of sensitivity for the detection of the first-named component :

Hydrogen in helium	0·07 per cent.
Helium in hydrogen	0·8 ,,
Hydrogen in argon	0·5 ,,
Argon in hydrogen	1·0 ,,

The pressure used varied from 0·1 to 0·4 mm.

Wolfe and Duffendack (1939*a*) have devised a technique in which they use helium in excess as the carrier of the electric discharge and a small addition of argon as the internal control. They found that helium makes an ideal carrier gas for several reasons. Firstly, its rate of clean-up is negligible when cathodic sputtering is avoided, so that the pressure in the discharge tube remains sensibly constant. Secondly, its excitation and ionization potentials are higher than those of other gases, and thus it does not tend to suppress the spectra of other gases present. Thirdly, helium can readily be purified to a high degree before its use for analytical purposes. Lastly, it has a relatively simple spectrum not likely to be confused with that of other components of the mixture. The intensities of helium lines are, however, affected by the amounts of other gases present, so that it is not suitable for use as an internal control. On the other hand, argon does not suffer from this defect, and was therefore used for this purpose. In certain circumstances it is possible to use an external control consisting of a special calibrated helium lamp which has been described (1939*b*).

The analyses were carried out using the positive column of a simple glow-discharge tube with internal electrodes, having a quartz capillary 3 mm. in diameter. The discharge was excited by a high-voltage transformer, the current through the discharge being 25 ma. It was found that the best helium pressure was between the limits 2 and 8 mm., and a pressure of 0·01 mm. of argon was found to be satisfactory for most of the work. Analytical working curves have been determined for the following gases, the pressure range being given :

Hydrogen	0·0001 to 0·0075 mm.
Nitrogen	0·004 to 0·25 mm.
Oxygen	0·02 to 0·12 mm.
Carbon monoxide . .	0·001 to 0·1 mm.

With nitrogen and carbon monoxide a band edge was used for comparison of intensities instead of a line ; no difficulty was experienced in doing this.

An interesting problem involving qualitative analysis has been described by Ryde and Huddart (1923), who investigated the nature of gas-bubbles occurring in glass. They evolved a technique for liberating the gas, and by a spectroscopic test for the presence of nitrogen distinguished between bubbles generated by chemical action and those introduced by mechanical processes.

§ 246. Group (2).—One of the most important gases in this group is carbon dioxide, which occurs so frequently in the gases resulting from industrial operations. Under the conditions obtaining in a sealed spectrum tube (stagnant gas) carbon dioxide is dissociated under the discharge, and emits the characteristic spectrum of carbon monoxide. If carbon dioxide is present and carbon monoxide is absent, then an estimate of the amount present can be made by the method of Wolfe and Duffendack for carbon monoxide given *above*. When both oxides are present and it is desired to determine each separately, it may be possible to remove the carbon dioxide by condensing in a side tube cooled with liquid air and thus determine the monoxide. A second experiment to determine the total oxides of carbon then gives the result desired. Another method of determining carbon dioxide spectroscopically is given later. This problem has been discussed by Lucian and Kautz (1934), who studied the gases evolved when iron, enamel, and enamelled iron, respectively, are heated inductively *in vacuo*. The gas samples were collected and sealed off in small spectrum tubes. The gases detected were hydrogen, water vapour, oxides of carbon, and nitrogen. These workers did not, however, differentiate between carbon monoxide and carbon dioxide evolved in their experiments.

In addition to the difficulty already mentioned of distinguishing between the oxides of carbon, a further complication arises in that these common gases may, under certain conditions, emit very uncommon spectra. An interesting example of this occurred recently during an investigation made at the Research Laboratories of the General Electric Company, Limited, Wembley, England. An unusual type of glow discharge (which cleaned up rapidly) could be produced under special conditions in certain tungsten-filament vacuum lamps which were under investigation. Spectrographic examination revealed a band system which was finally identified as the comet-tail band system of carbon monoxide, conditions for the production of which have been discussed by Merton and Johnson (1923). This identification was sufficient to determine the origin of the gas. This instance is a good example of the influence of the pressure and of the excitation conditions on the spectrum produced.

Lundegårdh (1930; 1934, p. 133) has determined the carbon dioxide in atmospheres by a spark method. The gas was passed slowly through a glass vessel, a spark being passed between electrodes of gold or platinum and observed through a quartz window. The carbon dioxide was estimated by comparing the intensity of the carbon line 2478·5 A. with that of the silver line 2477·3 A., silver occurring as an impurity in the gold electrode. Similarly with the platinum electrodes, the carbon line 2296·9 A. was compared with the palladium line 2296·5 A., palladium occurring in the platinum.

Heyes (1935) has used a similar method for the analysis of gas mixtures using a condensed spark between aluminium electrodes.

§ 247. Group (3).—Fluorine has formed the subject of a number of spectrographic investigations. The presence of fluorine in opal glasses has been detected by Ryde and Yates (1926), who mixed the sample with a little pure calcium oxide, and used the arc method of excitation. The characteristic and sensitive calcium-fluoride band at 5290 A. was used to indicate the presence of fluorine in the sample.

Churchill (1931) has used a similar method to detect the presence of fluorine in water supplies, and Petrey (1934) has extended the work to make quantitative determinations. Papish, Hoag and Snee (1930) have made use of the method to detect fluorine in gems and other minerals.

Paul (1936) has devised another method for the determination of fluorine. This involves the preparation of silicon tetrafluoride from the sample, and the uniform dissemination of this product in a small melt of a lead-borate glass, which is then examined spectrographically. The fluorine in the original sample is then deduced from the strength of the silicon lines in the spectrum of the glass.

§ 248. Group (4).—McAlister (1936) has developed a spectral absorption method for measuring carbon dioxide concentration. The region 4·2 to 4·3 μ. is chosen because almost all the gases and vapours commonly found in air except carbon dioxide are transparent to this radiation. An infra-red spectrometer is used with a vacuum thermocouple as the detector; the calibration is quite simply carried out by plotting galvanometer deflections corresponding to samples having known concentrations of carbon dioxide. For concentrations up to 0·10 per cent. of carbon dioxide, a path length of 86 cm. was used, and correspondingly shorter path lengths for greater concentrations. With the arrangement used, a deflection of 1 mm. represented 0·0001 per cent. of carbon dioxide. This method of determination is said to be as sensitive as the best chemical method, in addition to being much more rapid and less liable to error.

APPENDIX I.

UNITS AND DEFINITIONS.

Definition of Wavelength and Wave-number (Fowler, 1922).-- The position of a line in the spectrum is most generally indicated by the wavelength (λ) of the vibration which produces it. The unit of wavelength is the Ångström unit, or *angstrom*, as it is now called. It was intended to equal 10^{-10} metre, and is accordingly often called the *tenth-metre*. It is also equivalent to 10^{-8} cm., or 0·0001 μ., μ. being the *micron* or thousandth of a millimetre.* Wavelengths in the visible spectrum range from about 3900 A. to 7600 A. (A. being the modern abbreviation for the angstrom).† For the long waves in the infra-red, however, μ. is often taken as the unit, so that 12,500 A., for example, would be indicated by 1·25 μ.

The wavelength scale was introduced by Ångström in 1869, and until about the year 1900 wavelengths were referred to his determinations as standards. In the course of time, however, they have been measured with increasing accuracy, and the latest measurements, based on interferometer determinations, were for a time indicated by the letters I.A. (*international angstroms*),‡ which are the wavelengths in dry air at 15° C. and 760 mm. pressure.

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* A thousandth of a micron (a millionth of a millimetre) is often wrongly denoted by $\mu\mu$. The notation given in the following table, however, is more logical, and covers an extended range :

$$\left.\begin{array}{lcl} 1\text{ m.} & = & 1000\text{ mm.} \\ 1\text{ mm.} & = & 1000\,\mu. \\ 1\mu. & = & 1000\text{ m}\mu. \\ 1\text{ m}\mu. & = & 1000\,\mu\mu. \\ 1\,\mu\mu. & = & 1000\text{ m}\mu\mu. \end{array}\right\} ;\ \text{or}\ \left\{\begin{array}{lclcl} 1\text{ mm.} & = & 0{\cdot}001\text{ m.} & & \\ 1\mu. & = & 0{\cdot}001\text{ mm.} & & \\ 1\text{ m}\mu. & = & 0{\cdot}001\,\mu. & = & 10\text{ A.} \\ 1\,\mu\mu. & = & 0{\cdot}001\text{ m}\mu. & = & 10\text{ x.} \\ 1\text{ m}\mu\mu. & = & 0{\cdot}001\,\mu\mu. & & \end{array}\right.$$

† To-day one must extend these limits. Wavelength 3650 A. is regularly used in the visual calibration of certain double monochromators, while in the red wavelengths up to 9000 A. can be seen under favourable conditions.

‡ Since all modern tables are in international angstroms, it is now customary to indicate the international angstrom simply by " A." For further information on wavelengths see Twyman and Smith (1931).

In connection with spectral series, whether of emission or of absorption spectra, it becomes important to specify the positions of lines either in *oscillation frequencies* or by *wave-numbers*. The most fundamental figures are the oscillation frequencies, since these are not changed when the medium is changed. But the determination of frequency requires an exact knowledge of the velocity of light, and it is more convenient to use the wave-number or number of waves per centimetre *in vacuo* ; thus

$$\text{Wave-number} = \frac{10^8}{\lambda \text{ in angstroms}},$$

λ being here the wavelength *in vacuo*. The word *fresnel* is sometimes used to denote the unit of frequency :

$$1 \text{ fresnel} = 10^{12} \text{ vibrations per second.}$$

Unit of Capacity.—The unit of capacity is called the *farad* (F.), and is the capacity of a condenser which is charged to a potential of one volt by one coulomb of electricity. Expressed in electromagnetic units, 1 farad $= 10^{-9}$ c.g.s. unit. This is found to be much too large for ordinary purposes, and consequently the unit commonly employed is one-millionth part of this, called the *microfarad* ; 1 μf.* $= 10^{-15}$ c.g.s. unit.

Unit of Inductance.—The unit of inductance is called the *henry* (H.). A circuit has an inductance of one henry when an opposing electromotive force of one volt is induced in it by a variation in the inducing current of one ampère per second. This unit also is too large for practical purposes, and inductances are commonly given in *millihenries* (mh.*).

Both of these units have the dimensions of a length, and can therefore be expressed in centimetres. To convert a capacity given in centimetres to microfarads, divide by 900,000 ; to convert an inductance given in centimetres to millihenries, divide by 10^6.

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* Capital letters (F. and H.) are often employed instead of the lower-case letters used in this book.

APPENDIX II.

ADDITIONAL NOTES.

Improvements in Apparatus for producing Electric Sparks for use in Spectrochemical Analysis (Zeiss, 1939).—The improvements claimed in this patent specification, although shown in connection with an interrupted spark, do not appear to be necessarily limited to use therewith. The claims are for apparatus having a plurality of spark gaps connected in series and traversed by the same discharge current, but the spark gaps other than the one which is used for the radiation are bridged with either resistances, inductances, or condensers. It is stated, however, that it is preferable to use an ohmic resistance rather than capacity or inductance. The effect is said to be that under these circumstances the entire charging voltage is concentrated, before the passage of the spark, at the unbridged spark gap at which the radiation is to take place. When, however, the spark has taken place in this one gap, the voltage at this unbridged gap falls to a low value, so that nearly the entire charging voltage is now spread across the bridged spark gaps, and the sparking voltages of these gaps can be controlled by giving these resistances, etc. appropriate values. As a result, it is stated, the sparking no longer depends on the haphazard presence of initiating electrons at each one of the gaps at the same time.

(The following ten abstracts are extracted, with permission, from "Metallurgical Abstracts (General and Non-ferrous)," 1939, Ser. II, **6**, *London: The Institute of Metals.)*

Rapid Testing of Aluminium and Magnesium Alloys by the Method of Visual Spectral Analysis (Striganow, 1937).—The results of the determination of

aluminium, copper, manganese, silicon,
chromium, magnesium, nickel, zinc

in fourteen aluminium and magnesium alloys by the conventional method of visual spectral analysis are shown by a spectrogram and a table.

Spectrochemical Analysis (Mackenzie, 1939).—This author describes the equipment, technique, and results obtained in testing zinc-base die-castings for traces of elements, such as aluminium, lead, magnesium, and tin.

Contribution to the Spectrographic Analysis of Aluminium Alloys (Wolbank, 1939).—A modified sparking device is described with reference to diagrams and the optimum sparking conditions, and details of its use in the spectrographic analysis of silicon-aluminium and copper-magnesium-aluminium alloys are given. A presparking period of 2·5 min. is recommended for the silicon alloys, and 1·5 min. for the copper-magnesium alloys. The lines the intensities of which are compared photometrically are as follows: Al 2568 A. with Al 2575 A. (as a check), Fe 2599 A., and Co 2580 A.; Al 2367 A. with Cu 2370 A.; and Al 3057 A. with Mg 2937 A., Mn 2949 A., Ti 3349 A., and Cr 3132 A. The mean errors should not exceed ± 4 per cent. of the absolute amount of each constituent.

Spectrographic Analysis of Tin (Stewart, 1939).—Previous studies of the quantitative spectrographic analysis of tin are discussed, and shortcomings are indicated. The use of a large quartz Littrow spectrograph in the logarithmic sector wedge method is described. The selection of excitation conditions for quantitative analysis by the spark technique is discussed, and data are given on the general procedure. The technique used to secure uniformity and accuracy in the preparation of standard alloys is described. The selection of spectrum lines for internal standards and the preparation of working curves are discussed. The use of the working curves is dealt with, and some general considerations regarding their shape are presented. Working curves for the estimation of antimony in concentrations of from 0·01 to 0·5 per cent., bismuth from 0·003 to 0·1 per cent., copper from 0·001 to 0·05 per cent., iron from 0·002 to 0·1 per cent., and lead from 0·01 to 0·5 per cent. in tin are illustrated. The method used in measuring spectrum lines is described, and the accuracy of the method is considered.

New Application of Emission Spectroscopy to Local Micro-analysis (Scheibe and Martin, 1939).—A type of electrical discharge is described which affects an area of only 0·02 mm. diameter on the metal surface; valves are used for generating and rectifying the spark discharge. The resulting spark, which is almost a point source, is substituted for the slit of a spectrograph, and traverses the surface of a sample whose movement is geared to that of the carrier of the plate on which the spectrum is recorded. In this way the variation of composition of the sample can be explored along a given straight line or spiral, and the resolving power of the method is varied by altering the speed ratio of the spark and plate. The limitations of the method as a means of detecting grain-boundary segregation are discussed theoretically, and its results are illustrated by tests on aluminium alloys in which the silicon and iron are irregularly distributed ; also by tests on a synthetic sample of laminated material. Apparatus for conducting these tests in an inert-gas atmosphere is described, as well as the use of a microscope in identifying the area under examination.

Observations on Spark Fatigue (" Abfunkvorgänge ") in the Spectrographic Analysis of Aluminium Alloys (Kaiser, 1939).—Changes in the spectrum during the first few minutes of sparking the electrodes are usual, and may give place to a stable condition before the exposure is made for analysis ; this effect (termed " spark fatigue " or " spark-out effect ") can be properly investigated only if the physical and electrical factors which may cause spark variations are strictly minimized. The duration of spark fatigue is roughly proportional to the area of the electrode affected by the spark. Curves of the relative intensity of certain pairs of magnesium and aluminium lines in alloy spectra, plotted against time, show different shapes for different lines and also for different magnesium concentrations. Standard conditions are selected for the determination of magnesium in aluminium alloys with reasonable accuracy. The influence of absorption of the light from one spark by the vapour remaining from a previous discharge is eliminated, and it is observed that the relative intensity of certain lines may vary in different regions of the spark gap. This is partly attributed to erosion of the electrode surface by the spark ; the cavities formed then concentrate the metallic vapour into separate columns traversing the spark gap instead of a uniform vapour cloud. This effect is connected with the form of the oxides produced on the metal surface during sparking, but as it varies with lines of differing atomic origin it has not yet been completely explained.

Spectrographic Analysis and its Application to Aluminium (Handforth, Whymper and Boulton, 1939).—The routine determination in an industrial laboratory of iron, magnesium, manganese, and silicon in aluminium alloys by the internal-standard method is described. Two operators in one shift can analyse sixty samples of duralumin for the four elements. The line intensities are compared by means of a microphotometer. Electrodes are prepared from samples cast with side members 3 in. long and 0·25 in. in diameter, and are solution-treated at 500° C. for 20 min., and quenched in water. For aluminium alloys, a condensed spark of 0·02 μf. is used with a secondary voltage of 10,000 v. and an inductance of 0·13 mh. A rotary interrupter is considered unnecessary. Tables are given which show excellent agreement between the results of spectrographic and chemical analyses, and some commercial spectrographic equipment is described and illustrated.

Spectral Analysis of Niobium and Tantalum (Creffier, 1938).—Optimum conditions (2 amp., 65 to 70 v., 30-sec. exposure with oxide on cathode) are described for the spectrographic determination of niobium and tantalum to an accuracy of 1·5 per cent.

Standard Slide for Qualitative Spectrochemical Analysis (Ting-Chao Chang, 1939).—The standard spectrogram slide is made by arcing Hilger's R.U. powder to which have been added small quantities of compounds of gallium, hafnium, rhenium, thorium, uranium, and the rare earths. This slide then contains the most persistent lines of all the elements detectable by the arc method. These are recorded in five groups; their wavelengths and classification are given in a table.

Influence of Impurities on Line Strength in Quantitative Analysis (Brode and Silverthorn, 1939).—A critical review of published information on this effect is followed by the results of an investigation of the disturbances produced by sodium, potassium, lead, magnesium, copper, and bismuth on the relative intensities of cadmium and zinc lines in a mixture of powders with an alumina-silica base. Only the last two elements produced significant effects, the magnitudes of which varied with the concentration, chiefly between 2 and 5 per cent., of the addition, and differed in sign for the two cases.

Bibliography of Spectrochemical Analysis (Smith, 1940).—A second edition of this work has been published in 1940. It contains up-to-date references to a number of publications, conveniently classified. It is selective before 1930; it includes very brief abstracts of most papers and covers the metallurgical field completely up to August, 1940.

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(*Names and page numbers in the Author Index are given in italics.*)

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Alexy, K., 37, 187.

Alexy, K.—See under "Eisenlohr, F."

Alleyne, Sir J. G. N., 275.

Allsopp, C. B., 59.

Allsopp, C. B.—See under "Twyman, F."

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Balmer, 42–48.

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Bauer, R., 178, 180, 219, 225, 235.
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Becker, A. L.—See under " Sawyer, R. A."
Becquerel, E., 19, 22.
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Bergsøe, P., 208.
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Bohr, N., 47, 48, 56.
de Boisbaudran, Lecoq, 34.
Bossuet, R., 109.
Bossuet, R., 1935, *Compt. rend.*, **200**, 1094.
Boulton, W. M., 328.
Boulton, W. M.—See under " Handforth, J. R."
Brackett, 46.
Braidech, M. M., 176.
Braidech, M. M., and Emery, F. H., 1935, *J. Amer. Waterworks Ass.*, **27**, 557.
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BRISTOW, C. A.—See under "Adcock, F."
Broca, 40.
Brode, W. R., 154, 156, 157, 329.
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Clark, W., 93.
Clermont, J., 230, 237, 284.
CLERMONT, J.—See under "Schleicher, A."
Coheur, F. P. and P., 210.
COHEUR, F. P. and P.—See under "Gerlach, W."
Creffier, J., 283, 329.
CREFFIER, J., 1938, *Natuurwet. Tijds.*, **20**, 63.
——.—See also under "Breckpot, R."
Crookes, W., 23, 34.
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CRUSE, K.—See under "Schubert, H."
Cyr, H. M., 300.
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Daguerre, L. J. M., 20.
Davis, C. H., 133, 165.
DAVIS, C. H.—See under " Bassett, W. H."
Desains, 29.
Desch, C. H., 174, 273.
Dobson, G. M. B., 89, 181, 182.
DOBSON, G. M. B., GRIFFITH, I. O., and HARRISON, D. N., 1926, *Photographic Photometry*, p. 21, London: Oxford University Press.
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DOETSCH, J.—See under " de Rubies, S. P."
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Dreblow, E. S., 144, 248.
DREBLOW, E. S.—See under " Harvey, A." and " Twyman, F."
Driffield, V. C., 90, 183.
DRIFFIELD, V. C.—See under " Hurter, F."
Duffendack, O. S., 94, 95, 121-123, 131, 135, 176, 177, 181-183, 320, 321.
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Dupré, 142, 144.
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Edmunds, G., 300.
EDMUNDS, G.—See under " Truesdale, E. C."
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EMERY, F. H.—See under " Braidech, M. M."
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FEARON, W. R.—See under "Webb, D. A."
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George, W. H., 93.
Gerlach, W., 58, 106, 115, 132, 133, 137, 139, 154, 156, 166, 167, 178, 179, 210, 215, 230, 231, 234, 238, 253, 275, 296.
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Gregory, E., 174.
Griffith, I. O., 89, 181.
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Grotrian, 46.
Günther, P. L., 319.
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Hase, T., 26.
Heidhausen, G., 274.
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Hitchen, C. S., 112, 135, 174, 177, 178, 182, 185, 188, 225, 243, 300.
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——.—See also under "Twyman, F."
Hoag, L. E., 322.
Hoag, L. E.—See under "Papish, J."
Horton, C. A., 58, 171.
Horton, C. A.—See under "Foster, J. S."
Huddart, R., 321.
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Leonard, A. G. G., 38, 39, 41, 70, 124, 126, 135, 161, 163, 164, 196.
LEONARD, A. G. G.—See under "Pollok, J. H."
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——, *T., 34.*
——, T.—See under "Reich, F."
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Silverthorn, R. W., 329.
SILVERTHORN, R. W.—See under "Brode, W. R."
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Smithells, C. J., 143.

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Snee, W. E., 322.
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Torres, O. R.—See under " Pierce, W. C."

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Wells, *207*.
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Whymper, H. W.—See under "Handforth, J. R."
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Wiley, F. H.—See under "Duffendack, O. S."
van der Willigen, V. S. M., *25*.
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Yates, D. E., 322.
Yates, D. E.—See under "Ryde, J. W."
Yensen, 258.
Young, Thomas, 3, 5, 9.
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Zehden, W., 133, 167, 203, 227, 232, 248, 287.
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Zeiss, Carl, 83, 130, 326.
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SUBJECT INDEX.

A

Abfunkeffekt, 216, 254, 328.
Absorption of light, 48.
Accuracy of spectrochemical analysis. *See* “Spectrochemical analysis.”
Acetylene - air flame spectra. *See* “Spectra.”
Aluminium, Anodic formation of, 221.
——, High-purity, 224.
——, Routine analysis of, 225.
——, Spectrochemical analysis of. *See* “Spectrochemical analysis.”
——, Titanium in, Effect of, 237.
—— alloys, Rapid testing of, 326.
—— ——, Specifications of, 226, 227.
—— arc, 223.
—— in steel, 270.
Analysis, Qualitative, 148-153.
—— of solutions, 159.
Angström unit, 324.
Animal and plant tissues. *See* “Tissues.”
—— diseases. *See* “Diseases of animals.”
Aniseed oil, Prism of, 7.
Anlaufkurve, 217.
Arc, 111-124.
——, A.C., 114.
——, Fluctuations in, 304.
——, High-voltage A.C., 121-123.
——, Interrupted, 115-118.
——, Magnesium, Care in running, 286.
——, Polarity of, Effect of, 114, 118.
——, Sensitiveness of, 113, 118-120, 121.
—— and spark, Relative advantages of, 144, 145.
—— —— —— spectra, 55.
—— cathode layer, 118.
—— discharge, Physical factors operative in, 123.
—— spectra. *See* “Spectra.”
Ashing. *See* “Methods.”
Atomic energy states. *See* “Energy states.”
Auxiliary spectrum. *See* “Methods.”

B

BALMER series. *See* “Series.”
Band spectra. *See* “Spectra.”
Beryllium, Detection of, in alumina mixtures and magnesium alloys, 237, 290.
Bibliography, 329, 330.
Blackening. *See* “Photographic plates.”
Bohr’s theory, 47.
Boiling, Subsurface, 273.
Books, 153-155.
Brackett series. *See* “Series.”
Brasses and bronzes. *See* “Spectrochemical analysis.”
Breckpot’s copper-oxide method. *See* “Methods.”

C

CADMIUM, High-purity, 239.
Cadmium-copper alloys. *See* “Spectrochemical analysis.”
Cæsium, Discovery of, 32.
Capacity, Unit of, 325.
Cathode layer. *See* “Arc.”
Cathode-layer method. *See* “Methods.”
Chill moulds. *See* “Heterogeneity, Reducing.”
Chill-casting, 218.
Collimator. *See* “Spectroscope.”
Condenser system for isolating middle of spark, 285, 286.
Condensing lenses. *See also* “Lenses.”
—— ——, Mirror instead of, 83.
—— ——, Sphero-cylindrical, 79.
—— ——, Use of, 80-83.
Continuous spectrum, 13.
Copper, Arsenic in, Effect of oxygen on. *See* “Spectrochemical anlaysis.”
——, Impurities in. *See* “Spectrochemical analysis.”
——, Tellurium in. *See* “Spectrochemical analysis.”
—— and its alloys. *See* “Spectrochemical analysis.”
—— oxide as base. *See* “Spectrochemical analysis” and “Methods.”
—— —— —— —— for mixtures. *See* “Methods.”
Correlation method. *See* “Methods.”
Coulomb, 325.

D

DAGUERREOTYPE plate, 21.
Deficiency diseases of animals. *See* “Diseases.”

Developer, Ageing of, 264.
Development, Effect of variation in time of, 264.
Diffraction gratings. *See* " Gratings."
Diffuse series. *See* " Series."
Direct photometry. *See* " Methods."
Diseases of animals, Mineral-deficiency, 206.
  Border pine, 207.
  Bush sickness, 207.
  Coast disease, 207.
  Enzootic marasmus, 207.
  Moor-cling, 207.
  Pine, 207.
  Swayback, 207.
  Teart, 207.
  Warfa, 207.
——— plants, Mineral-deficiency :
  Internal cork, 207.
  Bitter-pit, 207.
Dispersion, 1.
Doppler effect, 49, 61.
Duffendack's method. *See* " Methods."

E

Effect of metallurgical condition, 282.
Electrode holder, 79.
—— surface, Effect of sparking on, 255.
Electrodes, Casting. *See* " Heterogeneity, Reducing."
——, Cooled, of Neuhaus, 113.
——, Moving, 215.
——, Preparation of, 227, 234.
——, Rotating, 281.
——, Separation of, 262, 281.
——, Shapes of, 139, 227, 234, 265.
——, Upper, Effect of material of, 265.
——, Water-cooled, 289.
—— for small specimens, 140.
" Elektron " alloys, 287.
Emission lines, Metallic, 5.
Energy levels, Atomic, 46, 51.
—— states, Atomic, 46, 48.
—— ——, Stationary, 48.
—— ——, Transition, 46, 52.
Exploded-wire method. *See* " Methods."
External-standard method. *See* " Methods."

F

Farad, 325.
Feussner spark. *See* " Spark."
Films, Metallic. *See* " Methods."
Fine wires. *See* " Methods, Exploded-wire."
Fixation pairs. *See* " Spectrum lines."
Flame methods. *See* " Methods."
—— spectra. *See* " Spectra."
Fluorescence, 22.
Fluorine, Detection of, 193.
Fluorspar for lenses, 75.
Fraunhofer lines, 4, 5, 12.
Fundamental series. *See* " Series."

G

Gamma. *See* " Photographic plates."
Gases. *See also* " Spectrochemical analysis."
——, Sensitive lines of, 67.
—— from molten metals, 202.
Ghosts. *See* " Spectrographs, Grating."
Glass, English, 7.
Globule arc. *See* " Methods."
Gold. *See* " Spectrochemical analysis."
Grain-boundary effect. *See* " Heterogeneity."
Graphical calculator, Owens', 102.
Graphs for spectrochemical analysis, Plotting, 97, 102.
Grating spectrograph, Use of, 299.
Gratings, Diffraction, 3, 4, 21, 34, 65-70.

H

Hartmann diaphragm, 148.
Henry, 325.
Heterogeneity, 215, 266, 327.
——, Grain-boundary effect, 215, 328.
——, Macroscopic and microscopic, 215, 218.
——, Reducing, in casting, 306.
—— of electrodeposited nickel, 292.
Hilfsspektrum. *See* " Methods."
Homologous lines. *See also* " Spectrum lines."
—— ——, 57, 58.

I

Identifying elements, 148-153.
Impurities, Influence of, on line strength 329.
Inclusions, 202.
Indium, Discovery of, 34.
Inductance, Unit of, 325.
Industrial applications, 204.
—— uses of spectrograph, Early, 165.
Insta eyepiece, 278.
Interference of light, 4.
Internal standard. *See also* " Methods."
—— ——, 58.
Interrupted arc. *See* " Arc."
—— spark. *See* " Spark."
Ionization potential, 53.
Iron, Cast. *See* " Super-rapid analysis."
——, High-purity, 257, 258, 260.
——, " Wemco " research, 258.
—— foundry, Spectrograph in, 278.

K

Kirchhoff's law, 30, 60.

L

LAY-OUT of spectrographic laboratory, 219, 220.
Lead. *See* "Spectrochemical analysis."
Lengths of lines, Use of, in spectrochemical analysis. *See* "Methods."
Lenses, Condensing, 79.
——, ——, Spherical, 79.
——, ——, Sphero-cylindrical, 79.
——, Positioning, 79, 83.
Levels, Atomic. *See* "Energy levels, Atomic."
Line series. *See* "Series."
Liquids. *See* "Methods."
Lithium fluoride for lenses, 75.
Logarithmic sector. *See also* "Methods."
—— ——, 273.
—— ——, Stepped. *See* "Methods."
Lomakin's method. *See* "Methods."
Lyman series. *See* "Series."

M

MAGNESIUM. *See also* "Spectrochemical analysis."
—— alloys, Rapid testing of, 326.
—— arc. *See* "Arc."
Methods:
  Ashing, 143, 165.
  Auxiliary-spectrum, 167, 178.
  Breckpot's, 183.
  —— copper-oxide method, 184, 245.
  Cathode-layer, 82, 118.
  Concentration by electrolysis, 144.
  Copper oxide as base for mixtures, 184, 245.
  Correlation, 212.
  Direct photometric, 177, 210.
  Duffendack's, 95, 181, 293.
  Eisenlohr's, 187.
  Exploded-wire, 143.
  External-standard, 187.
  Flame, 109, 184.
  Globule, 185, 243, 292.
  Hilfsspcktrum, 167.
  Internal-standard, 37, 231, 246, 247, 292.
  ——, Photometer for, 166.
  ——, for gases, 319, 320.
  Liquids, Hollow graphite for, 175, 178.
  ——, Tube for sparking, 182.
  Lockyer's, 37.
  Logarithmic-sector, 170.
  ——, Factors governing accuracy of, 172.
  ——, Stepped, 171, 183, 283.
  ——, Use of, 170, 174, 177.
  Lomakin's (calibration by known specimens), 95, 177.
  Lundegårdh's, 109.
  Metallic films, 144.
  Nitchie's, 178, 282, 297, 304.
Methods:
  Occhialini's (by length of lines), 174.
  Pellet, 165, 312.
  Photometry of lines, Direct, 177, 210.
  Powders, 184.
  Precipitates, 184.
  Ramage's, 184, 314.
  Rapid analysis, Curves for, 102, 183.
  Ratio-quantitative, 165, 312.
  Sensitive. *See also* "Arc, Sensitiveness of."
  ——, 178.
  Slavin's, 178, 188, 292.
  "Standard," 214, 225.
  Stepped-sector, 171, 183, 283.
  Stepped-slit, 181.
  Stepped-spectrum, 181, 183, 283.
  Steward and Harrison's, 184, 314.
  Synthesis of specimens, 164.
  Synthetic matching, 164.
  Total-energy, 188.
  Twin-spark, 187.
  ——, Barratt's, 169.
  Twyman and Hitchen's, 177.
  Variant-exposure, 209, 282.
  Water supplies, 176.
  Width of line, 187, 210.
Micro-analysis, Local, 327.
Micron, 324.
Microphotometer, 85, 176, 231.
——, Calibration of photographic plate for, 177.
——, Desiderata in, 103.
——, Use of, 87-103, 262.
——, —— ——, with stepped sector, 303.
—— in spectrochemical analysis, Review of work on, 104.
Minerals and ores, 161, 205.
Monochromatic light, 10.
Multiplicity, 56.

N

NICKEL, *See also* "Spectrochemical analysis."
——, Heterogeneity of electrodeposited, 292.
—— spectrum, Complexity of, 291.
Non-metallic substances. *See* "Spectrochemical analysis."
Normal atom, 55.
Notation and nomenclature, 62-64.

O

ORES. *See* "Minerals."
Owens' graphical calculator. *See* "Graphical calculator."
Oxy-coalgas flame spectra. *See* "Spectra."
Oxy-hydrogen flame spectra. *See* "Spectra."

P

Paschen series. *See* " Series."
Pellet method. *See* " Methods."
Persistent lines. *See also* " Spectrum lines."
—— ——, 38, 329.
Pfeilsticker arc. *See* " Arc, Interrupted."
Pfund series. *See* " Series."
Photographic plates, Blackening of, Definition of, 90.
—— ——, Gamma of, 91.
—— ——, Processing of, 92-94.
—— ——, Properties of, 90.
Photometry of lines, Direct. *See* " Methods."
Planck's constant. *See* " Radiation constant."
Plant and animal tissues. *See* " Spark, High-frequency " and " Tissues."
Plateholder. *See* " Spectrograph."
Platinum metals. *See* " Spectrochemical analysis."
Polarity. *See* " Arc."
Positioning lenses. *See* " Lenses."
Powders. *See* " Methods."
Precious metals. *See* " Spectrochemical analysis."
Precipitates. *See* " Methods."
Preliminary sparking, Effect of, 265.
—— treatment of specimens, 142.
Presparking, 215, 218, 228.
Principal series. *See* " Series."
Prism, Quartz. *See* " Spectrograph."
Processing, Rapid, 198.

Q

Quantum number, 51.

R

Radiation constant, Planck's, 48.
Radium. *See* " Spectrochemical analysis."
Raies sensibles, 39, 162.
—— *ultimes*, 39, 57, 152, 162, 329.
Ramage's method. *See* " Methods."
Rapid analysis, Curves for. *See* " Methods."
Ratio powders, 313.
Ratio-quantitative Method. *See* " Methods."
Refractive indices of glasses, 5.
Resonance potential, 53.
Reversal. *See also* " Spectrum lines."
——, 60.
R. U. powder, 152.
Rubidium, Discovery of, 34.
Rutherford atom, 47.
Rydberg's constant, formula, and law, 49.

S

Schwarzung, 91.
Scrap, Examination of, 203.
Segregates, 202, 267.
Selection rules, 51.
Self-reversal, 60.
Sensibles, Raies. *See* " Spectrum lines."
Sensitive lines. *See* " Spectrum lines."
—— —— of gases. *See* " Gases."
Sensitiveness. *See also* " Arc."
——, Increase of, by concentration, 142, 144.
—— of spectrochemical analysis, 196.
Series, Balmer, 42.
——, Brackett, 46.
——, Diffuse, 49.
——, Fundamental, 51.
——, Line, 42.
——, ——, Rydberg's formula for, 46.
——, Lithium, 43, 48-53.
——, Lyman, 46.
——, Paschen, 46.
——, Pfund, 46.
——, Principal, 49.
——, Sharp, 49.
Sharp series. *See* " Series."
Silver. *See* " Spectrochemical analysis."
Silver-chloride paper, Scheele's, 3.
Single spark. *See* " Spark."
Singlets, 57.
Slag, 216.
Slavin's method. *See* " Methods."
Slit, Illumination of. *See* " Condensers."
——, Width of, 72, 73, 286, 287.
Slits. *See* " Spectrograph."
Sodium lines, 5.
Solar spectrum. *See* " Spectrum."
Spark, 124-141.
——, Condensed, 124, 329.
——, Effect of capacity and inductance on, 124-132.
——, Feussner. *See also* " Spark, Interrupted."
——, ——, 130, 179, 274.
——, High-frequency, 132, 137.
——, Interrupted, 129-132, 180, 219, 272.
——, Liquids in, 135-137.
——, Modified device for, 327.
——, Oscillatory nature of, 125.
——, Point, for traversing surface of sample, 327.
——, Powders in, 134.
——, Powerful, 129.
——, Preferential effect of inclusions in, 268.
——, Single, 180.
——, Simple condensed, oscillating, or resonant, 129.
——, " Standard " circuit for, 127, 262.
——, Tandem, 133.
—— generator, 219.
—— spectra. *See* " Spectra."

Sparking circuit, Improvements in, 326
—— ——, “Standard,” 127, 262.
—— ——, Vincent and Sawyer's, 272.
Spark-out effect, 254.
Spectra, Acetylene-air, 108.
——, Arc, 111-124.
——, Atlas of, Lecoq de Boisbaudran's, 34.
——, Band, 59.
——, Flame, 55, 107.
——, Gas, 25, 202, 318.
——, Molecular, 33, 59.
——, Oxy-coalgas and oxy-hydrogen, 108.
——, Spark, of salts, 25.
Spectral series. *See* “Series, Line.”
Spectrochemical analysis, Accuracy of, 195, 228, 229, 267.
—— ——, Bibliography of, 329.
—— ——, Control of materials by, 274.
—— ——, Copper oxide as base in, 184, 245.
—— ——, Discovery of, 13, 27.
—— ——, Effect of metallurgical condition on, 282.
—— ——, Errors in, Causes of, 180, 262, 263.
—— ——, Limitations of, 193.
—— ——, Qualitative, 201, 329.
—— ——, Quantitative, First attempt at revival of, 37, 38.
—— ——, ——, Influence of impurities on line strength in, 329.
—— ——, ——, Recommended technique for, 101.
—— ——, Routine, 200, 328.
—— ——, Scope of, 193.
—— ——, Standard slide for, 329.
—— ——, Super-rapid, 271.
—— ——, Variety of uses of, 198.
—— ——, Visual, 237, 275-278, 289.
—— —— in archæology, 208.
—— —— —— art, 208.
—— —— —— criminology, 208.
—— —— —— metallurgy, 199, 201, 214.
—— —— of aluminium, 221.
—— —— —— —— alloys, 231-239, 327, 328.
—— —— —— —— ——, Lithium in, 236.
—— —— —— —— ——, Rapid visual, 326.
—— —— —— —— ——, Spark-out effect in, 328.
—— —— —— —— —— by solution, 235, 236
—— —— —— animal tissues. *See* “Tissues.”
—— —— —— argon-nitrogen, 319.
—— —— —— brasses and bronzes, 246.
—— —— —— cadmium, 239.
—— —— —— cadmium-copper alloys, 248.
—— —— —— carbon dioxide, 321, 322.
—— —— —— —— monoxide, 320.
—— —— —— carrier gas, 320.
—— —— —— clays, 199.
—— —— —— copper, Arsenic in, Effect of oxygen on, 245.
—— —— —— ——, Impurities in, 243.
—— —— —— ——, Tellurium in, 244.
—— —— —— —— and its alloys, 241.
Spectrochemical analysis of copper-cadmium alloys, 248.
—— —— —— films, 199.
—— —— —— fluorine, 322.
—— —— —— foodstuffs, 199, 201.
—— —— —— gases, 318-323.
—— —— —— gold, 249-253, 256.
—— —— —— grass, 210.
—— —— —— helium, 319.
—— —— —— hydrogen, 319, 320.
—— —— —— iron, 257.
—— —— —— krypton, 319.
—— —— —— lead, 278.
—— —— —— —— alloys, 278-286.
—— —— —— magnesium alloys, Beryllium in, 290.
—— —— —— —— ——, Rapid visual, 326.
—— —— —— —— and magnesium alloys, 286-290.
—— —— —— minerals, 205.
—— —— —— nickel and nickel alloys, 290-293.
—— —— —— niobium, 329.
—— —— —— nitrogen, 320.
—— —— —— non-metallic substances, 203, 312-323.
—— —— —— organic chemicals, 191, 209.
—— —— —— oxygen, 320.
—— —— —— plant tissues. *See* “Tissues.
—— —— —— platinum, Sulphur in, 296.
—— —— —— —— metals, 293-296.
—— —— —— precious metals, 253, 256.
—— —— —— precipitates, 199.
—— —— —— radium, 296.
—— —— —— refractories, 199.
—— —— —— silver, 297.
—— —— —— steel, 260, 278.
—— —— —— ——, Alloy, 268.
—— —— —— ——, Aluminium in, 270.
—— —— —— tantalum, 329.
—— —— —— tin, 297, 327.
—— —— —— vitreous substances, 199.
—— —— —— xenon, 319.
—— —— —— zinc and zinc alloys, 297-311, 327.
Spectrograms, Taking and interpreting, 147.
Spectrograph, Choice of, 70.
——, Early industrial use of, 165.
——, Effect of temperature on, 76, 77.
——, Grating, 65.
——, ——, Advantages and disadvantages of, 66-70.
——, ——, Ghosts in, 66, 69.
——, Intermediate quartz, 71.
——, Large quartz, 77.
——, Lenses of, 75.
——, Lining up light-source of, 146.
——, Makers of, 83, 84.
——, Medium, 72.
——, Plateholder of, 76.
——, Prism of, 75.
——, Quartz, 23, 25, 72-79.
——, Slit of, 72.

Spectrograph, Small, 71.
— , Vacuum, 67.
— — , Wavelength scale for, 76.
Spectrometer, Constant-deviation, 40.
— — , Visual, 65, 203, 275.
Spectroscope, Collimator, First use of, 23.
— , First, 5, 6.
— , Kirchhoff and Bunsen's, 31, 33.
Spectrum, Actinic, 17.
— , Colour of, 1, 4.
— , First photographs of a, 19.
— , — — photography of, 11.
— , Infra-red, 2.
— , Solar, 4.
— , Spark, 16, 81, 124-145, 326, 328.
— , — —, First observation of, 5.
— , Star, First observation of, 5.
— , Ultra-violet, 3, 17.
— , — —, Photography of, 25.
—, — — solar, 22.
— , Wheatstone's drawings of spark, 16.
— enlarger, 151.
— lines, Characteristic groups of, 153.
— — , Fixation pairs of, 167.
— — , Homologous, 81, 166.
— — , Long and short, 81.
— — , Persistent, 161.
— —, *Raies ultimes*, 39, 57, 152, 162
— —, Reversal of, 27.
— — , Sensitive (*raies sensibles*), 39, 162.
— — , Spark, 81.
— — , Tables and charts of. *See* "Tables."
Speed of spectrochemical analysis. *See also* "Spectrochemical analysis, Super-rapid."
— — — , 197, 269.
Spherical lenses. *See* "Lenses, Condensing."
Sphero-cylindrical lenses. *See* "Lenses, Condensing."
Standard alloys, Test for, 310.
Stark effect, 61.
Stationary states. *See* "Energy states, Stationary."
Steel, 260, 278.
— —, Alloy, 268.
Steeloscope, 203, 275.
Stepped sector. *See also* "Methods."
— — , 230, 303, 304.
— slit. *See* "Methods."
— - spectrum. *See* "Methods."
Steward and Harrison's method. *See* "Methods."
Strength, Influence of impurities on line, 329.
Striæ in glass, 7.
Subsurface boiling. *See* "Boiling."
Sulphating ash, Advantage of. *See also* "Methods."
— — — —, — — — , 299.
Sun, Metals in, proved by spectroscopy, 30.
Super-rapid analysis, 271.
Synthesis of artificial grass, 210.
— — — specimens. *See* "Methods."
Synthetic matching. *See* "Methods."

T

TABLES and charts, 155-158.
Tandem spark. *See* "Spark."
Techniques, 159-192, 209-213.
Tenth-metre, 324.
Terms, Even, 53.
— , Odd, 53.
Tesla coil. *See also* "Spark, High-frequency."
— — in gas analysis, 320.
Thallium, Discovery of, 34.
Tin. *See* "Spectrochemical analysis."
Tissues. *See also* "Spark, High-frequency
— , Animal, 206.
— , Plant, 206.
Total-energy method. *See* "Methods."
Transition states. *See* "Energy states, Transition."
Triplets, 57.
Twin-spark, Barratt's. *See* "Methods."

U

Ultimes, Raies, 39, 57, 152, 162, 329.
Ultra-violet, Limit of vision in. *See also* "Spectrum."
— — , — , 19, 324.
Undulatory theory, 4.
Units and definitions, 324.

V

VACUUM region, Sensitive lines in, 68.
— spectrograph. *See* "Spectrograph."
— tubes, Use of, in analysis of metals. *See* "Spectrochemical analysis of sulphur" and "Spectrochemical analysis of gases."
Variable results, Causes of. *See* "Spectrochemical analysis, Errors in."
Variant-exposure method. *See* "Methods."

W

WATER supplies, Spectrochemical analysis of. *See* "Methods."
Wave theory, 4.
Wavelength, Determination of, by interpolation, 104, 149, 150.
——, First calculator of, 3.
——, Measurements of, 3, 24.

Wavelength, Measuring, 150-153.
——, Rowland's, 35.
——, Standard, 81.
——, Unit of, 324.
—— of Newton's colours, 4.
—— scale. *See* "Spectrograph."
"Wemco" research iron. *See* "Iron, 'Wemco.'"
Widths of lines, Analysis by. *See* "Methods."

Z

Zinc and zinc alloys. *See* "Spectrochemical analysis."

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